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Discussions of the Faraday Society

No. 3, 1948

INTERACTION OF WATER
AND
POROUS MATERIALS

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A GENERAL DISCUSSION

ON

INTERACTION OF WATER AND POROUS MATERIALS

GENERAL INTRODUCTION

A General Discussion on the Interaction of Water and Porous Materials was held in the Department of Physics of the University College, Southampton (by kind permission of Prof. A. M. Taylor) from the 31st March to the 2nd April, 1948. In the absence of the President, Prof. A. J. Allmand, F.R.S., the Chair was taken by Prof. E. K. Rideal, F.R.S., and later by Prof. N. K. Adam, F.R.S. About 125 members and guests were present; among the distinguished overseas guests Prof. E. K. Rideal welcomed the following:

> Prof. and Madame C. J. F. Böttcher (Leiden), Dr. H. C. Brinkman (Amsterdam), Dr. J. J. Broeder (Amsterdam), Prof. E. Fauré-Fremiet (Paris), Prof. and Madame J. H. van den Honert (Leiden), Dr. M. Joly (Paris), Dr. A. Klinkenberg (The Hague), Mr. K. J. Nieuwenhuis (Delft), Dr. G. Th. Phillippi (The Hague), Dr. and Mrs. I. Razouk (Cairo), Dr. Eleanor Slifer (Iowa City), Dr. Börje Steenberg (Stockholm), Dr. T. Swarbrick (The Hague) and Dr. I. Wark (Melbourne).

Before the Discussion was formally opened, the Chairman paid a warm and generous tribute to the magnificent work of the late Honorary Secretary, Mr. G. S. W. Marlow, on behalf of the Faraday Society over a period of twenty-one years, and members and visitors were invited to stand in silence as a tribute to his memory.

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I. FUNDAMENTAL ASPECTS

Introductory Paper

By N. K. Adam

PRINCIPLES OF PENETRATION OF LIQUIDS INTO SOLIDS

Received 18th February, 1948

Porous solids may range in texture all the way from solids whose substance is impermeable to liquid, but are traversed by capillary tubes of diameter substantially greater than the range of molecular attraction, to solids which have no capillaries or pores in the ordinary sense, but whose substance is capable of dissolving, molecularly, some of the liquid. The theory of penetration into capillaries is well understood, at least when these are of approximately uniform bore. When the bore of the capillaries decreases so far that the molecules on one side begin to attract those on the other, right across the bore, the problem of penetration gradually changes to the problem of solution of a liquid in a solid; and the theory appears to be very inadequately developed.

In all cases, ultimately, the penetration is controlled by the adhesion between molecules; in the case of penetration into macroscopic capillaries, the relative magnitudes of the adhesion of liquid for solid, and of the self-cohesion of the liquid, together with the diameter of the capillaries, determine the effective pressure driving the liquid into the capillaries. When the bore of the capillaries is so small that there is appreciable adhesion between the opposite walls, the self-cohesion of the solid must also become important.

Capillary Penetration

The fundamental formulae are, as is well known,[1] easily deduced from the existence of free surface energy at any interface between phases of different composition. This free surface energy arises from the inward attraction of the underlying molecules on those in the surface, and since a surface possessing free energy contracts when free to do so, the free surface energy is also called surface tension. Dupré's equation,

$$W_{SL} = \gamma_S + \gamma_L - \gamma_{SL} \quad . \quad . \quad . \quad . \quad (1)$$

relates the work of adhesion W_{SL}, required to separate unit area of solid and liquid in contact, to the surface tensions γ_S, γ_L, γ_{SL}, of solid, liquid, and solid liquid interface respectively. Combining with the equation for equilibrium for a liquid resting at a "contact angle" on the solid,

$$\gamma_S = \gamma_{SL} + \gamma_L \cos \theta \quad . \quad . \quad . \quad . \quad (2)$$

Young's equation (1805)

$$W_{SL} = \gamma_L(1 + \cos \theta) \quad . \quad . \quad . \quad . \quad (3)$$

results. This gives the fundamental relation between the adhesion of liquid to solid, and the contact angle, showing that there is a finite angle if the adhesion of liquid to solid, W_{SL}, is less than the self-cohesion of the liquid, $2\gamma_L$; and zero angle if the adhesion of liquid to solid becomes equal to, or greater than, the cohesion of the liquid.

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[1] cp. Adam, *The Physics and Chemistry of Surfaces* (1941), pp. 178, 413, and ref. there quoted.

When a liquid enters a capillary of small radius, a curved meniscus will be set up unless the contact angle is exactly 90°, producing a difference in pressure $P_1 - P_2$ on the two sides of the liquid surface,

$$P_1 - P_2 = \gamma_L\left(\frac{1}{R_1} + \frac{1}{R_2}\right) \quad . \quad . \quad . \quad (4)$$

R_1, R_2 being the principal radii of curvature; for a capillary of circular section and radius r, this becomes a " penetrating pressure "

$$P = \frac{2\gamma \cos \theta}{r} \quad . \quad . \quad . \quad . \quad (5)$$

The contact angle varies, however, with the tendency of the liquid to move along the solid surface, being a maximum when the liquid is advancing over a dry surface. Calling the " advancing " angle, obtained when the meniscus is moving slowly into the capillary, θ_A, the pressure driving a liquid spontaneously into a capillary of circular section whose walls are parallel to the axis (i.e., uniform section), is

$$P_i = \frac{2\gamma \cos \theta_A}{r} \quad . \quad . \quad . \quad . \quad (6)$$

P_i is positive when the meniscus is concave, i.e., when $\theta_A < 90°$.

For penetration, the advancing angle θ_A is the relevant contact angle; the pressure required to expel the liquid from the capillary is

$$P_o = \frac{2\gamma \cos \theta_R}{r} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where θ_R is the " receding " angle made when the liquid is receding from a previously wetted surface. Since $\theta_A > \theta_R$, $P_o > P_i$; a greater pressure is required to expel a liquid from a capillary, than the pressure which drives it in spontaneously.

The difference between the advancing and receding contact angles, or " hysteresis " of the contact angle, can be large; up to 60° on smooth surfaces has been recorded and much larger values on rough surfaces. Hysteresis seems to be larger for water than for organic liquids, but it exists with these also. It does not yet appear fully understood; perhaps there is no single explanation for all cases. Since $\theta_A > \theta_R$, eqn. (3) shows that the adhesion of liquid for the previously wetted solid exceeds that for the dry solid. Hysteresis has been variously ascribed to films on the dry surface, less easily wetted than the main substance of the solid, and removed by the liquid; to overturning of the surface molecules of the solid, to bring their more hydrophilic parts to the surface, when water touches the surface; and to the formation of multi-molecular clusters of liquid molecules on the solid surface, after the liquid has receded (Cassie [2]). It has long been known that the receding angle tends to decrease as the liquid remains in contact with the solid, probably because the solid soaks up or dissolves, in its surface layers, some of the liquid. Cassie [2] states that receding angles are much more variable than advancing angles; on the other hand, Bartell and Wooley [3] found that the receding angle with glass or silica, and organic liquids, was easier to reproduce than the advancing angle. The hysteresis in the case of organic liquids and glass may well be due to the receding angle being that obtained when the surface pores in the glass are filled with liquid, the advancing angle depending on the extent to which these pores are dry, or partially filled with liquid. After continued heating in the presence of vapour of the liquid, the advancing angle tends to become equal to the receding.

[2] Cassie, *Trans. Faraday Soc.*, 1948 (this Discussion).
[3] Bartell and Wooley, *J. Amer. Chem. Soc.*, 1933, **55**, 3518.

The minimum contact angle obtainable is zero, and for "receding" angles this figure is not uncommon, though it is less often attained with advancing angles. The question, what is the maximum possible advancing angle, on a *smooth* surface, is an important one for all waterproofing problems. It is probably between 110° and 120°; Ablett[4] made most careful measurements of the contact angle between air, water and paraffin wax, finding 113° for the advancing angle, equal by (3) to a work of adhesion of water to dry wax of 44·2 ergs/sq. cm., at 20° ($\gamma_l = 72{\cdot}8$). Long-chain compounds with polar groups at one end of their molecules, such as stearic acid, show angles very nearly as large (Adam and Jessop[5]), because the surface consists of hydrocarbon groups, with the polar, water-attracting groups well buried below a layer of hydrocarbon. Baxter and Cassie[6] record an angle of 120° on a proofed wool fibre. Since measurements of the work of adhesion between liquid paraffins and water also give values of the order 40 ergs/sq. cm., a greater work of adhesion being obtained for all other organic liquids, it seems unlikely that, at any rate with organic substances, real contact angles greater than 120° can exist.

It is well known, however, that when the surface is rough, i.e. contains minute elevations and depressions, much greater apparent contact angles can be obtained. Coghill and Anderson[7] obtained advancing angles of about 160° with powdered galena thickly sprinkled on a plate, and Adam (1927) found a similar angle for rough surfaces of pigment particles on a plate, coated with stearic acid. Conmar Robinson[8] obtains about 160° for the advancing angle of water on some types of leather. Generally, roughness simply increases the difference between the real contact angle (on a smooth surface of similar attraction for water) and 90°; if the real angle is less than 90°, some penetration into pits occurs, so that liquid touching the rough surface is in contact with liquid of its own composition, over part of the surface, thus increasing the average work of adhesion over the whole surface; if the real angle is greater than 90°, air is entrapped in the hollows, over which there is then no adhesion to overlying water so that the average work of adhesion is less than over a smooth surface. Wenzel[9] gives the relation,

$$\cos \theta' = \sigma \cos \theta \quad . \quad . \quad . \quad . \quad . \quad (8)$$

θ' being the apparent angle on the rough surface, and σ the ratio between the real area of rough solid accessible to a liquid, and the apparent area, which expresses quantitatively the way in which roughness enhances the difference between the real angle and 90°. Baxter and Cassie[6] found, for a (presumably smooth) proofed wool *fibre*, $\theta_A = 120°$, $\theta_R = 60°$; for the comparatively rough proofed *yarn*, $\theta'_A = 157°$, $\theta'_R = 20°$, figures in excellent agreement with Wenzel's eqn. (8), putting $\sigma = 1{\cdot}86$.

Cassie and Baxter[6, 10] have investigated the case of fabrics in which cylindrical fibres are spaced in various orderly arrangements, with vacant spaces up to a few times the diameter of the fibres, showing that apparent contact angles up to nearly 160° will be obtained on fabrics with threads appropriately spaced, on which the true angle does not exceed 120°; apparent angles on the cloth, up to about 170°, are theoretically possible if the yarns are rough surfaces with an apparent angle (advancing) of 150°. Thus by roughness in the yarns, combined with accurately maintained spacing between them in the cloth, a chemical proofing which would on a smooth surface give an advancing angle of, say, 113° can be made to give an almost perfectly water-repellent surface with advancing angle 160°–170°. The superlative water-repellence of ducks' feathers is due, not to any miraculously water-repellent wax, but to the well-designed structure in which the barbules are kept apart at nearly the theoretically ideal distance.

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[4] Ablett, *Phil. Mag.*, 1923, **46**, 244.
[5] Adam and Jessop, *J. Chem. Soc.*, 1925, 1865.
[6] Baxter and Cassie, *J. Textile Inst.*, 1945, **36**, 167.
[7] Coghill and Anderson, *U.S. Bureau Mines* Tech. Paper, 1923, **262**, 47.
[8] Conmar Robinson, *Trans. Faraday Soc.*, 1948 (this Discussion).
[9] Wenzel, *Ind. Eng. Chem.*, 1936, **28**, 988.
[10] Cassie and Baxter, *Trans. Faraday Soc.*, 1944, **40**, 546.

Pores are rarely capillaries of uniform bore. An approximation to the pressure required to force water through the pores of a fabric may be obtained by treating the yarns as " rough " surfaces, and using the apparent advancing angle θ'_A on the yarn in (6) (Baxter and Cassie, also Bartell *et al.*[11]). Because cotton yarns are rougher than those of Nylon and similar synthetic fibres, the same proofing gives greater resistance to water penetration with cotton cloth than with Nylon cloth of similar weave.

The theory of penetration into capillaries of complex shape is difficult. Often aggregates of powders are treated formally as equivalent to capillaries and eqn. (6) and (7) used to deduce the contact angle from the observed pressure P_i produced by the penetrating liquid, or P_0, required to expel the liquid. An independent determination of the radius r of the " equivalent capillary " is required; this may be done by measuring the viscous resistance to flow of a liquid through the thoroughly soaked powder (Bartell, 1926, Carman[12]). Such methods have their uses, but they may conceal our present ignorance of how the liquid actually finds its way into the nooks and crannies of a solid, where the pores suffer frequent and abrupt changes of size and shape.

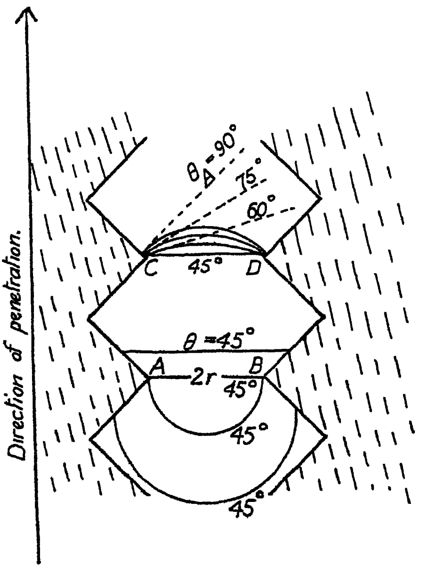

FIG. 1 *a*

Simple geometrical considerations given below show that the penetration pressure P_i will decrease, perhaps even become negative, when the meniscus has to find its way past a constriction in a pore. Fig. 1 *a* shows a tube of corrugated section, for simplicity taken as a figure of revolution about the axis, the walls being inclined at an angle 45° to the vertical axis. If the advancing contact angle is 45° (lower part of figure), P_i will be $\frac{2\gamma}{r}$ before passing the constriction where the radius is r, and zero after passing. If $\theta > 45°$ (upper part of figure), P_i becomes negative at the moment of passing, so that unless external pressure is applied, the meniscus will not pass the constriction. Fig. 1 *b* shows the more general case (but still a figure of revolution) where the walls are inclined at φ_1 to the horizontal below the constriction EF and at φ_2 above. Before passing, the radius of curvature of the meniscus R_1 is $\frac{r}{\sin(\theta_A + \varphi_1)}$; after passing, the radius R_2 is $\frac{r}{\sin(\theta_A - \varphi_2)}$, so that the penetration pressure changes from $\frac{2\gamma \sin(\theta_A + \varphi_1)}{r}$ to

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[11] Bartell, Purcell and Dodd, *Trans. Faraday Soc.*, 1948 (this Discussion).
[12] Carman, *Trans. Faraday Soc.*, 1948 (this Discussion).

$-\frac{2\gamma \sin(\theta_A - \varphi_2)}{r}$ on passing the constriction. P_i becomes negative if $\theta_A > \varphi_2$. This effect of constrictions is analogous to the "edge effect" found by Coghill and Anderson in flotation of solids of angular shape (cp. ref. [1], p. 194); but the constriction need not be sharp, as the effect depends on the slopes φ_1 and φ_2 of the walls, not on the abruptness of change of slope.

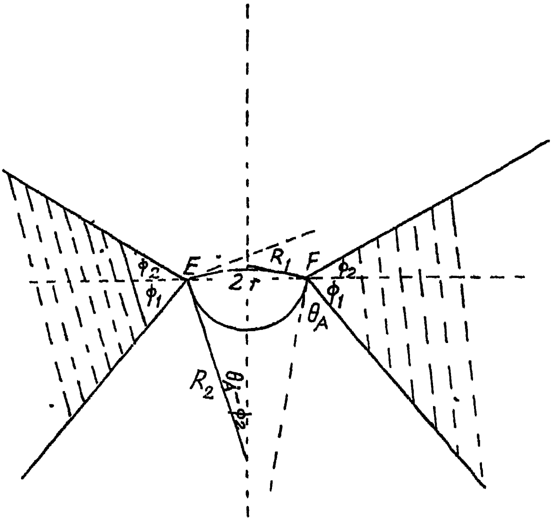

FIG. 1 *b*

I can attempt only qualitative considerations on the mechanism of penetration, when the bore of the capillaries is small enough for the attraction of the walls to extend right across them. Liquid in the pores will everywhere be within the range of attraction of the walls. The question whether the surface tension has its normal value in such a capillary has been discussed in connection with capillary condensation,[13] but no definite conclusions appear to have been reached. The following considerations indicate that the potential energy of a molecule in the surface of a liquid, in a very narrow tube, will be less than in a free liquid surface. The surface molecule A (Fig. 2) is attracted inwards by the liquid below it in the tube, and this attraction is presumably the same as that from a similar column of free liquid. There is also the downward attraction of the solid walls below the level XY of the surface molecule A, and the upward attraction of the walls above XY, which cancel each other in a vertical direction. Hence the work required to bring A from the interior of the liquid to the surface is less than in a free liquid surface, by the attraction which would be exerted downwards on A, by liquid in the space actually occupied by the walls of the tube below XY. Hence the surface tension is decreased by the attraction of the walls of the tube.

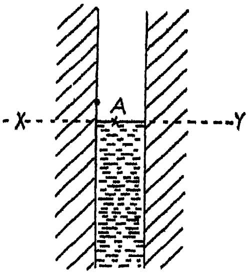

FIG. 2

In such a very narrow tube it is difficult to speak of a definite contact angle, since the kinetic agitation of the liquid surface must make the surface indefinite in position to one or two molecular diameters, which is the same order of magnitude as the range of molecular attraction and therefore as the diameter of the tube (a horizontal line is therefore used in Fig. 2 to suggest the level, though not the probable form, of the surface). Eqn. (5) for the penetrating pressure seems to lose its meaning owing to the indefiniteness of θ.

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[13] Brunauer and Emmett, *Adsorption of Gases* (1943), Vol. I, 126.

Diffusion of molecules along the walls of extremely narrow tubes, within the range of molecular attraction, probably plays an important part in penetration into pores of this order of magnitude. Barrer brings evidence[14] that the rate of penetration of gases into zeolites, where the pores are of molecular dimensions, is controlled by surface diffusion on the pore walls. Stamm[15] uses a similar conception to describe the movement of water in wood. Penetration into very narrow pores may cause them to widen, and Hirst[16] suggests that this may be one of the causes of hysteresis in adsorption (hysteresis of the contact angle may well be another). If the liquid (or vapour) entering the pore wedges the walls open so that, when full, the walls are beyond each other's range of attraction, the entering liquid must do work in overcoming this attraction between solid walls. This work is not recovered, at least with rigid walls, on removal of the liquid or vapour adsorbed on the solid walls. Charcoal expands when adsorbing gases: Bangham[17] ascribes this to the surface pressure of mobile adsorbed films in the charcoal pores, these films being of the "gaseous" type. There is plenty of other evidence that adsorbed films, if held by van der Waals' forces, are very mobile.

When there is appreciable penetration of the liquid, by molecular solution, into the walls of the pores, one may anticipate that a liquid will tend to form a smaller contact angle with the walls than if there were no such "soaking" into the walls; this will assist penetration along the pores, according to (5). When definite pores are absent, and penetration is wholly by molecular solution, the attraction between solid and liquid molecules must be great enough to separate liquid molecules from each other, and to achieve some degree of separation also of the solid molecules from each other as the liquid molecules penetrate between them.

How far the "secretion" of water, or maintenance of a definite gradient of thermodynamic potential (or concentration or pressure), with movement of water against this gradient, will prove to be explicable in terms of the principles applicable to non-living pores, is difficult to predict at present. Several instances of such water secretion are described in this Discussion.

ADDENDUM TO PAPER (*communicated*, 12th April, 1948).

By polymerising methyl methacrylate round a Zn former, and dissolving out the Zn with HCl, a tube with zigzag walls similar to that in Fig. 1 was made; the minimum radius r was 0·135 cm. The angle φ_1, and φ_2 were each about 47°; the advancing contact angle θ, on a flat plate of this material, is of the order 85°. The penetrating pressure before passing a constriction, calculated according to the formula in the paper is 802; after passing, -665 dynes/sq. cm. The difference is 1467 dynes/sq. cm., about 15 mm. head of water, assuming the normal surface tension of water. When the walls of the tube were dry, and a reservoir of water communicating with the lower end of the zigzag tube was gradually raised, the meniscus in the tube rose rapidly to the first constriction, then stuck; on raising the reservoir about 10 mm., the meniscus passed at once to the next higher constriction. The rise continued in this jerky manner, from constriction to constriction, right up the tube. The difference between the experimental value of 10 mm., and the calculated value of 15 mm. may possibly have been due to contamination decreasing the surface tension of the water in the narrow tube.

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[14] Barrer, *Trans. Faraday Soc.*, 1944, **40**, 206, 555; 1948 (this Discussion).

[15] Stamm, *Trans. Faraday Soc.*, 1948 (this Discussion).

[16] Hirst, *Trans. Faraday Soc.*, 1948 (this Discussion).

[17] Bangham *et al.*, *Proc. Roy. Soc. A*, 1930, **130**, 81; 1932, **138**, 162; 1934, **147**, 152, 175; 1938, **166**, 572; *J. Chem. Soc.*, 1931, 1329.

CONTACT ANGLES

By A. B. D. Cassie

Received 27th January, 1948

1. Contact Angle and Surface Structure

When a drop of liquid is placed on a solid surface it may remain as a drop of finite area, or it may spread indefinitely over the surface. The condition for spreading is that the energy gained in forming unit area of the solid-liquid interface should exceed that required to form unit area of the liquid-air surface; or if γ_{SA} is the solid-air interfacial energy, γ_{SL} is that of the solid-liquid interface, and γ_{LA} is that of the liquid-air interface, then for spreading:

$$\gamma_{SA} - \gamma_{SL} > \gamma_{LA} \qquad . \quad . \quad . \quad . \quad (1)$$

When this inequality is not fulfilled, the drop remains finite in size and an equilibrium contact angle exists. The condition for equilibrium requires that, in the absence of gravity effects, the contact angle θ between the liquid and the solid surfaces is given by [1]:

$$\cos \theta = \frac{\gamma_{SA} - \gamma_{SL}}{\gamma_{LA}} \qquad . \quad . \quad . \quad . \quad (2)$$

Eqn. (2) shows that the cosine of the contact angle gives the ratio of the energy gained in forming unit area of the solid-liquid interface to that required to form unit area of the liquid-air interface. It should be emphasised that (2) is a geometrical relation, and the unit areas are plane geometrical areas.

The surface area of a liquid-air interface is unique and may always be identified with its plane geometrical area, but the surface area of a solid-liquid interface depends very much on the condition of the solid surface. Thus, if a solid surface is roughened so that unit plane geometrical area has an actual surface area σ times that of the "smooth" surface, the energy gained in forming the solid-liquid interface will be $\sigma(\gamma_{SA}-\gamma_{SL})$, and the contact angle, θ', for the rough surface will be given by [2]:

$$\cos \theta' = \frac{\sigma(\gamma_{SA} - \gamma_{SL})}{\gamma_{LA}} \qquad . \quad . \quad . \quad . \quad (3)$$

The angle θ' has been termed the "apparent" contact angle in contrast with the "real" angle θ of eqn. (2), because close inspection of a rough surface would always reveal the "real" contact angle on any element that could be regarded as smooth. It might thus be said that any surface has two advancing and receding contact angles, the apparent angles which are shown on casual inspection of the intersection of the solid and liquid surfaces, and the "real" angles seen by a close inspection. The measurement of contact angle is, therefore, somewhat arbitrary, for one might pursue this argument to molecular dimensions when the surface would appear rough and heterogeneous. Fortunately, for practical purposes, it is possible to have a reasonable division of surfaces into "smooth" and "rough" and so attach some meaning to the "real" and "apparent" contact angles, but unless the smooth surface is a reproducible one, the "real" contact angle will not be reproducible. It is doubtless the difficulty of reproducing a "smooth" surface that gives rise to so many different published values for the contact angles of a given liquid and solid.

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[1] Adam, *The Physics and Chemistry of Surfaces*, 3rd ed. (Oxford, 1941), p. 179

[2] Wenzel, *Ind. Eng. Chem.* 1936, **28**, 988.

Despite the uncertainty of absolute values of contact angles, eqn. (2) and (3) do give a useful relationship between measurable roughness and contact angle. Thus, a contact angle of more than 90° is increased by roughening the surface, and one of less than 90° is lessened by roughening.

The analysis for a rough surface is readily extended to heterogeneous surfaces. If unit geometrical area of a surface has an actual surface area σ_1 of contact angle θ_1, and an area σ_2 of contact angle θ_2, the energy E gained when the liquid spreads over the unit geometrical area is

$$E = \sigma_1(\gamma_{S_1A} - \gamma_{S_1L}) + \sigma_2(\gamma_{S_2A} - \gamma_{S_2L})$$

Where γ_{S_1A}, and γ_{S_1L} are interfacial solid-air and solid-liquid tensions for the σ_1 areas, and γ_{S_2A} and γ_{S_2L} are the interfacial tensions for the σ_2 areas. The contact angle θ'' for the composite surface is given by:

$$\cos\theta'' = \frac{E}{\gamma_{LA}} = \sigma_1 \cos\theta_1 + \sigma_2 \cos\theta_2 \ . \qquad . \qquad . \qquad (4)$$

The most important heterogeneous surface in practice is the porous surface. In this case the solid surface area is σ_1, and σ_2 represents air spaces; γ_{S_2A} is then zero, and γ_{S_2L} becomes γ_{LA}, or

$$\cos\theta'' = \sigma_1 \cos\theta_1 - \sigma_2 \ . \qquad . \qquad . \qquad . \qquad (5)$$

Eqn. (5) has already been given[3] and a number of applications have been discussed.[4] It is an equation that can be verified experimentally, and it appears to fit empirical data well to within the limits of error.[3] The presence of pores, represented by σ_2, always increases the contact angle θ'', and it is possible to have apparent contact angles as large as 150° when the "real" contact angle is around 90°. The equation is particularly useful in discussing natural and artificial porous clothing surfaces, where the aim is to make σ_2 as large as possible consistent with rain drops failing to penetrate the structure.

2. The Problem of Receding Contact Angles

The theories of contact angles for rough and heterogeneous surfaces are essentially geometrical, and they can be used for capillary calculations that would otherwise be intractable. Calculation of the pressure required to force water between the yarns in a fabric is an example of the use of eqn. (5). It is a very complex problem when considered in terms of the contact angle of individual fibres, but it is relatively easily solved by use of apparent contact-angle methods.[4] The calculated pressure in this case agrees to within the limits of error with the measured penetration pressure.

It is, of course, only the advancing contact angle that is involved in penetration pressure and, in general, problems that involve only the advancing contact angle appear to give agreement of theory and experiment. The receding contact angle cannot be used with the same confidence, and it is probably true to say that no phenomenon in textiles that involves receding contact angles has been satisfactorily explained. The source of the difficulties with receding contact angles is easily traced: it is their instability; the fibre-water receding contact angle may have one value on first contact with water, but this value decreases rapidly with continued immersion of the fibre in water.

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[3] Cassie and Baxter, *Trans. Faraday Soc.*, 1944, **40**, 546.

[4] Baxter and Cassie, *J. Text. Inst.*, 1945, **36**, T67.

The instability of receding contact angles is the real bar to progress in the theory of water repellency, and it may be worth while discussing once again the problem of the difference between the advancing and receding angles. The type of surface that gives finite contact angles is of considerable importance in this respect. The work of adhesion W of the liquid to the smooth solid is given by[1]:

$$W = \gamma_{LA}(1 + \cos \theta) \quad . \quad . \quad . \quad . \quad (6)$$

and one notes that when θ is finite, W is less than $2\gamma_{LA}$, or the work of adhesion is always less than that of liquid to liquid. Condensation of the saturated vapour in a form identical with the bulk liquid would not be expected unless W was equal to, or greater than, $2\gamma_{LA}$, or unless θ was zero. But it is well known that vapours are adsorbed on to surfaces that show finite contact angles, and the liquid must show its finite contact angle against the adsorbed layer rather than against the clean solid surface. Bangham and Razouk[5] have discussed contact angles from this point of view, and pointed out that the adsorbed films must be different from the liquid in bulk.

The isotherms of the vapour molecules adsorbed on to finite contact-angle surfaces are usually of the sigmoid type, which are now identified with multimolecular adsorption. This adsorption postulates low-energy localised sites, so that at low vapour pressure, molecules are adsorbed exothermically on to the sites; as the vapour pressure increases molecules are supposed to condense on to those already in the low-energy sites, giving rise to multimolecular adsorption, which is in excess of the Langmuir adsorption. The problem of multimolecular adsorption is to account for the excess condensation. If the contact angle is finite, the average work of adhesion must be less than that of liquid to liquid and condensation could not take place at saturation or lower vapour pressures without an increase of entropy compared with that of the liquid in bulk. The increase of entropy comes from the distribution of the adsorbed molecules.[6] [7] If X molecules of a total number N, are adsorbed singly on to localised sites, their partition function is[8]:

$$Q_s = \frac{B\,!}{(B - X)\,!\,X\,!}\left[j_s\ e^{-E_s/kT'}\right]^X \quad . \quad . \quad (7)$$

Where B is the total number of localised sites, E_s is the potential energy of an adsorbed molecule relative to one in the bulk liquid, and j_s is the partition function for a molecule in a site.

The partition function for the $(N - X)$ condensed or "liquid" molecules is[9]:

$$Q_L = \frac{(N - 1)\,!}{(N - X)\,!\,(X - 1)\,!}\left[j_L\ e^{-E_L/kT'}\right]^{(N-X)} \quad . \quad . \quad (8)$$

Where E_L is the potential energy of a condensed molecule relative to one in the bulk liquid, and j_L is its partition function; j_L is usually assumed to be identical with that for a molecule in the bulk liquid.

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[5] Bangham and Razouk, *Trans. Faraday Soc.*, 1947, **33**, 1459.
[6] Cassie, *Trans. Faraday Soc*, 1945, **41**, 450.
[7] Cassie, *Trans. Faraday Soc.*, 1947, **43**, 615.
[8] Anderson, *J. Amer. Chem. Soc.*, 1946, **68**, 688.
[9] Hill, *J. Chem. Physics*, 1946, **14**, 263.

The increase of entropy for the adsorbed molecules comes from the configurational partition function $\frac{(N-1)!}{(N-X)!\,(X-1)!}$ of the "liquid" molecules. This function represents the number of ways that $(N-X)$ identical molecules can be divided into X separate compartments with no restrictions as to how many there are in any one compartment. The essential point for the present discussion is that the compartments must be *separate*: or each compartment must represent a distinct cluster of molecules. If the compartments are not distinct, and they are not distinct in a continuous film, the configurational partition function becomes unity, and the molecules will evaporate when E_L is positive, which is the requirement for the existence of a finite contact angle. Hence, any multimolecular layer on a surface which shows finite contact angles must be in the form of distinct clusters of molecules; it cannot be a continuous film.

The surfaces immediately ahead of an advancing contact angle and behind a receding angle are, therefore, heterogeneous: they consist of clusters of liquid separated by areas of liquid-repellent solid surface. The observed contact angle will, therefore, be a composite one of the form θ'' given by (4). The contact angle θ_1 with the clusters will be zero, and that with the solid surface θ_2 may have any large value; there is, in fact, no theoretical objection to θ_2 being 180°, or to W of eqn. (6) being zero for the areas of endothermic reaction of the liquid with the surface.

If this description of a surface adjacent to a contact angle is correct, the difference between the advancing and receding angles must be due to different values of σ_1 and σ_2 for an unwetted surface and for one from which a liquid is receding; or the size of the liquid clusters must be different for the two surfaces when exposed to saturation vapour pressure. Now, eqn. (8) does show that such a difference is possible at one vapour pressure, or at one value of Q_L; for E_L contains the surface energy of the clusters which will depend on their size, and it also contains the entropy term which depends on the number of clusters. If the receding liquid leaves some clusters which cover more than one localised site, the average size of the clusters will be increased, E_L will be decreased, and the corresponding increase in Q_L will be compensated by the reduction in the number of clusters, which reduces the configurational entropy term. The larger clusters will require a greater adsorption of molecules, which corresponds to the well-known adsorption hysteresis effect, and they will give larger values of σ_1 and smaller values of σ_2. Thus, a liquid advancing on to a "dry" surface may encounter a large number of small discrete clusters which give a small value of σ_1, whilst a receding liquid may leave large clusters with a comparatively large value of σ_1; the advancing contact angle will, therefore, be large, and the receding one small.

This is, of course, very much a qualitative description of the difference between advancing and receding contact angles, and it is essential to determine whether or not the terms in eqn. (8) have the magnitudes necessary for the proposed mechanism. E_L can be deduced from the adsorption isotherm, and Anderson [8] gives values ranging from 175 to 300 cal./mole which are of the order of magnitude one might expect from the surface energies of clusters, each containing a few molecules. E_L for water adsorbed by keratin is 550 cal./mole, but this value is complicated by the swelling energy of the keratin.[10] The average size of the clusters at saturation vapour pressure can also be deduced from the isotherms,[7] and they may be shown to range from 2 molecules per cluster for water adsorbed by keratin to 5 per cluster for water adsorbed by TiO_2.[8] The clusters are, therefore, quite small and their surface energies should be large as is indicated by Anderson's data.

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[10] Cassie, *Symp. Soc. Dyers Col.* (Bradford, 1946), p. 90.

The configurational entropy contribution to the free energy F_M is given by the negative of the logarithm of the appropriate terms in (8) or, neglecting unity in comparison with N and X, by:

$$\frac{F_M}{RT} = -N \log N + (N - X) \log (N - X) + X \log X \quad . \qquad (9)$$

If X is $\frac{1}{a}N$, so that each cluster contains on the average a molecules, the free energy per mole is given by:

$$\frac{F_M/N}{RT} = \left(1 - \frac{1}{a}\right) \log \left(1 - \frac{1}{a}\right) + \frac{1}{a} \log \frac{1}{a} \quad . \quad . \qquad (10)$$

Eqn. (10) gives F_M/N as -415 cal./mole at 300° K. for 2 molecules per cluster, -335 cal./mole for 4 per cluster, and -305 for 5 per cluster. These values do not balance the potential energy term E_L because of other factors in the partition function expressions (7) and (8), but they are of the same order of magnitude, which is what is required for different sizes of clusters to give the same value of the free energy per mole. Thus, increasing the cluster size from 4 to 5 increases the free energy by 30 cal./mole so far as configurational entropy is concerned, whilst the surface energy might be expected to decrease to $\left(\frac{4}{5}\right)^{2/3}$ of its original value; if the original value was 300 cal./mole, the value at 5 molecules per cluster would be 265 cal./mole, or the decrease in free energy due to the increase in cluster size would be 35 cal./mole, which very roughly balances the increase due to the configurational change.

It might be thought that this argument could be extended to give one cluster, or a continuous film of adsorbed molecules; but one notes that the absolute value of the configurational entropy term is generally larger than the energy term, E_L; one cluster would reduce the entropy term to zero, whilst E_L can not be reduced to zero, so that a continuous film is not a possible state of the system.

One concludes that at saturation vapour pressure, the adsorbed molecules can vary in extent by assuming a number of different configurations which all lead to one value of the free energy per mole, and are, therefore, possible states of the system. If adsorption is obtained by increasing the vapour pressure, one cluster will form at each occupied localised site, and the configuration obtained at saturation vapour pressure will be unique; correspondingly, the advancing contact angle for a "dry" surface should be unique. But, when the liquid recedes from the solid surface, it may leave clusters which on the average cover more than one site; the amount adsorbed will then be greater than that on the surface ahead of the advancing contact angle, and σ_1 will be greater behind the receding angle than ahead of the advancing one, giving a small receding contact angle. There does not seem to be a unique configuration for the receding system, as one value of the free energy per mole can be obtained from a range of configurations; hence, the receding contact angle will not have a unique value, and this is, in fact, its most troublesome experimental property.

My thanks are due to Mr. B. H. Wilsdon, Director of Research, for his interest in this work, and to the Council of the Wool Industries Research Association for permission to publish this account.

Summary

The relationship of contact angles to surface structure is outlined. The difference between the advancing and receding contact angles is discussed in terms of the modern theory of multimolecular adsorption; this theory indicates that the advancing angle will be unique, whilst the receding one will generally be less than the advancing angle and need not have a unique value.

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Leeds, 6.

THE SPREADING OF A LIQUID OVER A ROUGH SOLID

By R. Shuttleworth* and G. L. J. Bailey†

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The spreading of a liquid over the surface of a solid is a complex phenomenon; the final position of the liquid at rest depends not only upon the surface energies of the liquid, the solid and the solid-liquid interface, but also upon the roughness of the surface and the manner in which the liquid is placed on the solid.[1] [2] Experimentally, spreading is studied by measuring the variation of the apparent contact angle φ, the angle between the general directions of the liquid and solid surfaces. If the solid is rough, this is different from the true contact angle θ, the angle between the liquid and solid surfaces at a particular point in the line of contact. In general, even when the liquid is at rest, the static value of the apparent contact angle φ_E depends upon whether the liquid has reached this position by advancing or receding over the solid, the advancing being always greater than the receding contact angle. The difference in the two values is called hysteresis.

Wenzel[3] was the first to discuss the influence of roughness on apparent contact angle. Hysteresis of the contact angle has previously been attributed to the adsorption on the solid, either of the liquid[4] or of a layer of foreign molecules.[5] In this paper the problem of the spreading of a liquid over a rough solid is considered in detail and it is shown that hysteresis of the contact angle will arise merely because of the inevitable roughness of solid surfaces and that it is not necessary to invoke any special mechanism of adsorption to explain it. However, in particular systems it is probable that adsorption contributes to hysteresis, and that the relative importance of the two effects can only be decided by experiment.

If gravity is neglected, the final position of the liquid at rest is one of stable or metastable equilibrium in which the total surface energy of the system is a minimum. Because of fluidity it is also necessary that the surface energy of the liquid surface (proportional to the area) be a minimum, subject to the constraints that the liquid volume be constant and that the liquid remain in contact with the solid over a certain (not necessarily plane) domain. The shape of the surface ABC, Fig. 1, which has the minimum area subject to these constraints, is obtained from the consideration that for any small arbitrary change of shape brought about by the elements of area dA being displaced in the directions of their normals by amounts dn, the total change of area is zero for a minimal surface or,

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[1] Adam, *Physics and Chemistry of Surfaces* (Oxford, 1941).
[2] Burdon, *Surface Tension and the Spreading of Liquids* (Cambridge, 1940).
[3] Wenzel, *Ind. Eng. Chem.*, 1936, **28**, 988.
[4] Bartell and Wooley, *J. Amer. Chem. Soc.*, 1936, **55**, 3515.
[5] Langmuir, *Science*, 1938, **87**, 493.

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$$\iiint \left(\frac{1}{r_1} + \frac{1}{r_2}\right) dA \,.\, dn = 0.$$

r_1 and r_2 are the principal radii of curvature at the point dA and the integration is carried out over all the liquid surface. However, since the total change of volume is zero,

$$\iiint dA \,.\, dn = 0.$$

Hence the minimal surface satisfies the differential equation

$$\frac{1}{r_1} + \frac{1}{r_2} = \text{const.} \qquad . \quad . \quad . \quad . \qquad (1)$$

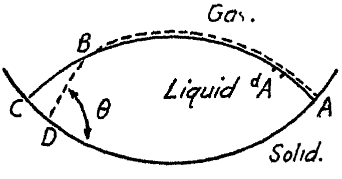

FIG. 1.

Thus, if the volume of the liquid and the domain over which it is in contact with the solid are specified, its surface is completely defined.

Similarly, when the drop is in equilibrium with the solid, any infinitesimal displacement of the line of contact of the three interfaces must produce zero change of energy. When the position of a portion of liquid-gas interface is changed from the equilibrium position BC to BD by rotation through an angle $d\theta$, the decrease of volume being compensated by a corresponding increase over BA, the total change of surface energy is zero. If curvature perpendicular to the plane of the paper is neglected

$$\left(S_S - S_{SL}\right)\frac{BCd\theta}{\sin\theta} - S_L\left\{\frac{BCd\theta}{\tan\theta} - O\left(\frac{BC^2 d\theta}{AB}\right)\right\} = 0,$$

S_S, S_L, S_{SL} being the energies per unit area of the solid, liquid and solid-liquid surfaces respectively. The position of B is arbitrary and therefore BC/AB can tend to zero and the final term be neglected. The equilibrium condition then reduces to

$$S_S = S_{SL} + S_L \cos\theta_E \qquad . \quad . \quad . \quad . \qquad (2)$$

If a volume V of a liquid is placed on a smooth plane solid with which its angle of contact is θ_E, equilibrium occurs when (1) and (2) are satisfied simultaneously. This is a spherical cap whose height h and radius r_1 are given by

$$V = \frac{\pi h^2}{3}\left(3r_1 - h\right) \qquad \text{and} \qquad h = r_1\left(1 - \cos\theta_E\right).$$

When a liquid is at rest on a rough solid, eqn. (1) and (2) must still be satisfied at all points on its surface and at the line of contact. In general, this necessitates that near the solid the liquid surface be ragged; but at distances from the line of contact large compared to the wavelength of the solid's roughness, the liquid surface will be smooth and inclined at an angle φ_E to the general direction of the solid surface. The value of the contact angle measured on a rough solid is φ_E; and by an extension of the previous treatment, the value of φ_E which gives the absolute minimum of the total surface energy is readily found. In Fig. 2, B represents a line on the liquid surface whose distance from the solid is so large that here the surface is smooth. When φ_E corresponds to minimum total surface energy the change of energy on displacing the surface from BC to BD is zero, the distance CD is supposed small compared to BD but large compared to the dimensions of the roughness. The change in energy of the liquid arises almost entirely from the change of area of the smooth portion of its surface (BD ′ — BC ′) per unit length. The increase in the solid-liquid interface after this displacement is rCD per unit length, where r is the ratio of true to apparent surface area of the solid. By the same argument as is used to derive eqn. (2),

$$S_S = S_{SL} + \frac{S_L}{r} \cos \varphi_L,$$

$$\text{or } \cos \varphi_E = r \cos \theta_L \quad . \qquad (3)$$

This formula was first derived, but in a less rigorous manner, by Wenzel.[3] Cassie and Baxter[6] pointed out that when the true angle of contact was greater than 90°, the liquid did not penetrate into the concavities of the roughness and that in this case Wenzel's formula must be modified by the inclusion of a further term.

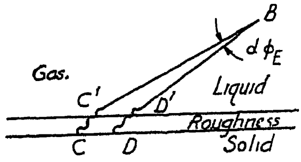

FIG 2.

When a liquid is placed on a solid surface so as to cover an arbitrary domain, the liquid-gas surface rapidly assumes a shape which satisfies (1). Then in general, θ the angle between liquid and solid does not satisfy (2) and the liquid spreads or recedes so as to cover a different solid domain, the liquid-gas surface continuing to satisfy the differential eqn. (1), but with different boundary conditions. Movement continues until simultaneously (1) is satisfied over all the surface and (2) over the line of contact at the edge of the solid domain. This will be an equilibrium position of minimum total surface energy, but it need not necessarily be the absolute minimum for which the apparent contact angle is given by (3). Subsidiary minima, as well as the absolute minimum, can exist so that positions of metastable as well as stable equilibrium are possible.

Two-Dimensional Roughness

Although, on solids whose roughness is of such a nature that metastable equilibrium is excluded, (3) gives the general direction of the liquid surface not too near the solid, the shape of the liquid surface in the immediate vicinity of the solid must depend upon the particular form which the roughness takes. In order to obtain a detailed picture of the shape of the liquid surface in the immediate vicinity of a rough solid, and to understand the processes of spreading, it is best to consider initially two-dimensional roughness; this has the form of a series of parallel grooves separated by ridges. Spreading over such a surface is anisotropic and will be discussed for directions parallel and perpendicular to the grooves.

(a) Spreading Parallel to the Grooves.—A liquid rises or falls in a capillary tube according to whether its angle of contact with the tube is greater or less than 90°; the height of rise or fall is limited only by gravity. A drop of liquid placed on a smooth solid in which there is a groove behaves in a similar manner: if, in equilibrium, the angle of contact is acute, a tongue of liquid will extend from the drop along the groove; if the angle of contact is obtuse, the reverse will occur and the liquid surface will be dented and not extend so far in the groove as it does on the smooth surface. The exact form of the tongue or dent will depend upon the geometry of the cross-section of the groove, but the deeper and narrower the groove, the more nearly it approximates to a capillary tube and the greater the effect. For small contact angles the liquid will flow to an unlimited length along the groove; when the angle is large and the groove deep and narrow, the liquid will nowhere touch the bottom.

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[6] Cassie and Baxter, *Trans. Faraday Soc.*, 1944, 40, 546.

This behaviour is best illustrated by considering the mathematically simple case in which the groove has the form of an isosceles triangle of height h and basal angle $(180° - 2\psi)$.

When a large drop rests on such a groove, the surface of the tongue of liquid must have an approximately zero curvature equal to that of the remainder of the drop, and be inclined at the equilibrium angle of contact to the walls of the groove. A solution which satisfies these conditions is that of a plane inclined to the horizontal at an angle α where

$$\cos \alpha = \cos \theta_E \sec \psi$$

This is not the complete solution because the plane would not join smoothly with the remainder of the drop: it seems that most of the tongue will have this form, but where the tongue merges into the drop the surfaces will have equal and opposite curvatures in perpendicular directions. The approximate length of the tongue is:

$$l = \frac{h}{\tan \alpha}.$$

Because of the definition of ψ, $\tan \psi$ is always positive so that the sign of l depends only upon whether θ_E is acute or obtuse. When θ_E is acute, the length of the tongue increases as ψ increases (as the groove becomes sharper) until when it becomes equal to θ the liquid spreads continuously up the groove to a length determined only by gravity.

When the solid is completely covered by identical isosceles grooves, the form of the liquid surface in the grooves and near the solid is that of a plane inclined to the horizontal at an angle α. This is otherwise obvious from (3), for with this type of roughness, $r = \sec \psi$.

When the solid surface contains only occasional grooves connected by plane portions, the presence of tongues makes the liquid surface near the solid ragged. The apparent angle of contact in the grooves α is less than that on the plane portions of the solid, but further from the solid the liquid surface is smooth and has a slope, intermediate between α and θ, given by (3).

In general, the section of the groove is not an isosceles triangle, but it can be regarded as being derived from one of angle $\psi_{\text{max.}}$ by a rounding of the corners, $\psi_{\text{max.}}$ is the maximum slope of the side of the groove. Because r, the roughness ratio, is less than $\sec \psi_{\text{max.}}$ this form of groove causes a smaller change in the apparent contact angle than does the corresponding triangular groove, and the tongues of liquid extend to a smaller distance in the grooves.

(b) Spreading Perpendicular to the Grooves.—In this case the line of contact is rectilinear and moves in a direction perpendicular to the length of the grooves. The problem is the spreading of an infinitely long cylinder of liquid, placed on a grooved surface with its axis parallel to the grooves. Initially, the angle φ between the liquid and the general direction of the solid is 180°, the liquid spreads so as to reduce φ, but for each value of φ the liquid surface remains a cylindrical segment. As spreading progresses, the height of the segment decreases and the radius increases, Fig. 3.

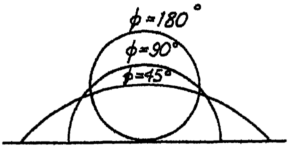

FIG. 3.

The roughness of the solid, i.e., the presence of grooves, causes the true contact angle θ to be less or greater than the apparent angle φ, according to whether the gradient of the solid at the line of contact is the same as, or opposite to, that of the liquid surface (Fig. 4, points A and B). The nature of the roughness is specified by the angles ψ' and ψ, the inclinations which the positive and negative slopes of the grooves make with the general direction of the solid. The maximum angles of slope are $\psi_{\text{max.}}$ and $\psi'_{\text{max.}}$ and the roughness is supposed to be such that these are always less than 90°. The true contact angle of the liquid with the negative slope is

$$\theta = \varphi - \psi,$$

and with the positive slope

$$\theta = \varphi + \psi'.$$

As the liquid spreads, the apparent contact angle, φ, decreases monotonically; θ, the true contact angle, has superimposed upon this same mean decrease a periodic variation of amplitude $\psi_{\text{max.}} + \psi'_{\text{max.}}$ which occurs each time the line of contact moves over a wavelength of roughness. Spreading ceases when θ falls to its equilibrium value θ_E, and this first occurs when

$$\varphi_E = \theta_E + \psi_{\text{max.}} \quad . \quad . \quad . \quad . \quad (4)$$

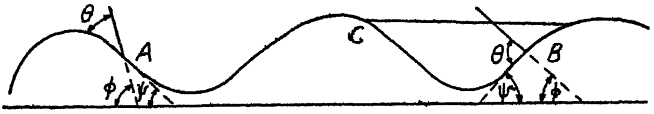

FIG. 4.

The line of contact is then at that portion of a groove where the gradient is a maximum; and the apparent contact angle is greater than the true contact angle by an amount $\psi_{\text{max.}}$ This value of φ is not the same as that predicted by (3), for although this is a minimum of the total surface energy, it is a subsidiary minimum of metastable equilibrium.

If the liquid be spread over the solid by some mechanical means, the apparent contact angle φ may be reduced to such an extent that the true contact angle is less than its equilibrium value θ_E. The liquid then spontaneously recedes until θ increases to θ_E. During recession the apparent contact angle increases monotonically whilst the true contact angle has superimposed upon this mean increase a periodic variation of amplitude $\psi_{\text{max.}} + \psi'_{\text{max.}}$ Recession ceases when the true contact angle first reaches its equilibrium value and

$$\varphi_E = \theta_E - \psi'_{\text{max.}} \quad . \quad . \quad . \quad . \quad (5)$$

The line of contact is then at a portion of the groove where the gradient is a maximum, and the apparent contact angle is less than the true by an amount $\psi'_{\text{max.}}$ This is another position of metastable equilibrium. It is therefore clear why on such a surface the advancing is greater than the receding contact angle, the hysteresis being $\psi_{\text{max.}} + \psi'_{\text{max.}}$

Other positions of metastable equilibrium occur for values of φ_E between the extremes of advancing and receding contact angle, but these cannot arise from the spontaneous spreading or recession of the liquid, but only from some form of mechanical spreading.

Eqn. (4) and (5) are respectively the boundary conditions for the surfaces of the advancing and receding liquids, for they define the gradient of the surface at the line when it intersects the steepest portion of the groove. When the advancing apparent contact angle is obtuse or the receding apparent contact angle acute, (4) and (5) are not always applicable; for there is the possibility that the planes defined by them could not form part of the liquid surface because they intersect the next ridge, as at C, Fig. 4. When this is so, the first positions of equilibrium will not be given by (4) and (5), but the advance or recession of the liquid will continue beyond this with the corresponding decrease or increase of the apparent contact angle. The final position of the liquid at rest will be the first metastable equilibrium position for which the predicted boundary conditions are such that the liquid surface clears the top of the next ridge. This will be for the advancing liquid when

$$\varphi_E = \theta_E + \psi_E,$$

and for the receding liquid when

$$\varphi_E = \theta_E - \psi'_E,$$

where ψ'_E and ψ_E are the gradients of the groove at the place where the liquid surface meets the solid, they are less than the maximum gradients.

In order that a large hysteresis exist between the advancing and the receding apparent contact angles, it is not sufficient merely to increase the maximum gradient of the groove; it is also necessary that the sides have a large gradient at a place whose distance from the top is small compared to the groove width. When the grooves are narrow at their points of greatest gradient, $\psi_E + \psi'_E$ will be small and there will be only small hysteresis.

Three-Dimensional Roughness

The roughness on the surface of a real solid will not be in the form of grooves but will probably be isotropic with the same properties in all directions. Two limiting forms of such surface texture occur: a plane covered by an array of hills standing on equal square bases, and the corresponding female surface of a plane covered by an array of square hollows. Spreading on the latter kind of surface would be of the same nature as spreading perpendicular to the grooves in the two-dimensional case; the angle of contact would be greater or less according to whether the liquid was advancing or receding. This hysteresis is greatest when the ridges between the hollows are steep and the widths of the hollows large compared to their depth.

Spreading on the male form of surface, in which valleys exist between the hills, is analogous to two-dimensional spreading parallel to the grooves; positions of metastable equilibrium do not arise, the apparent contact angle is given by (3) and is greater or less than the true contact angle according to whether the latter is obtuse or acute. Spreading will occur in the valleys between the hills so as to form projecting tongues of liquid, and if the angle of contact is sufficiently small it will proceed until they are full. The occurrence of spreading in the valleys excludes the possibility of metastable equilibrium, in which the line of contact lies on the slope of a ridge; but before the general line of contact can advance so as to reduce the apparent contact angle the valley in front must first fill with liquid. This viscous flow of the liquid in the narrow valleys will determine the rate at which spreading occurs.

Experiment shows that advancing and receding angles of contact may vary by so much as 60°, but that sometimes the liquid will slowly assume an equilibrium value which is the same for spreading and recession. Little is known of the texture of solid surfaces, but experiments on contact resistance indicate that even the smoothest solid surfaces have projections higher than 100 A. and these would be sufficient to explain the observed effects.

Summary

A liquid placed on an ideally smooth solid spreads until the total surface energy is an absolute minimum and the contact angle is uniquely defined. When the solid is rough, the value of the apparent contact angle at the absolute minimum of surface energy is different and is given by Wenzel's expression. In equilibrium, the liquid

surface near a rough solid must be ragged in order that it intersect the solid at the true contact angle. On solids, whose roughness is formed by isolated pits, subsidiary minima of total surface energy exist and hysteresis of contact angle arises because the liquid comes to rest at a different minimum after spreading and recession The inevitable roughness of solids is sufficient to explain hysteresis.

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THE MECHANICAL INTERACTION BETWEEN MOBILE INSOLUBLE ADSORBED FILMS, CAPILLARY CONDENSED LIQUID AND FINE-STRUCTURED SOLIDS

BY W. HIRST

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Provided that the adsorption isotherm of a vapour on a homogeneous fine-structured solid is reversible, the free energy lowering per unit mass of the solid is given to a high degree of approximation by the integrated form of the Gibbs-Duhem equation.[1]

$$G_A{}^0 - G_A = \frac{RT}{M}\int_0^p \frac{m_B}{m_A}\,d\log_e f \quad . \quad . \quad . \quad (1)$$

where $G_A{}^0$ is the Gibbs free energy per gram of pure adsorbent,
G_A is the Gibbs free energy per gram of adsorbent when in equilibrium with the vapour at pressure p and fugacity f,
m_A, m_B are the masses of adsorbent and adsorbate respectively, and
M is the molecular weight of the adsorbate.

The free energy lowering derived in this way is very nearly correct no matter what the method of interaction between solid and vapour may be. In particular, if the solid is rigid and incapable of dissolving the vapour, the free energy lowering is completely accounted for by the lowering of its *surface* free energy and $\frac{RT}{M}\int_0^p \frac{m_B}{m_A}\,d\log_e f = F\Sigma$* where F is the (Helmholtz) free energy lowering per unit surface, and Σ is the surface area per gram.

Should the solid swell on adsorption of a vapour, the free energy lowering of the solid may not now be equated to the surface free energy lowering only, since some energy will be stored in the solid as work of expansion. Accordingly,

$$G_A{}^0 - G_A = F\Sigma - W$$

where W is the work of expansion. It should be noted that Σ may no longer be constant. The magnitude of W will depend on the physical properties of the solid, notably on its mechanical properties, and on the mechanism whereby swelling occurs. It is to be expected, for example, that more work would be expended in stretching the actual substance of the solid than in merely separating its structural units. The adsorption isotherm alone however does not provide the evidence whereby a separate evaluation of $F\Sigma$ and W may be made, nor does it, by itself, enable the mechanism of swelling to be determined.

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* This equation is exact.

[1] Bangham, *Nature*, 1944, 154, 837.

There are additional uncertainties of interpretation when, as often happens with swelling adsorbents, the isotherms exhibit hysteresis, for the question arises how to determine the decrease in free energy of the system when the isotherm does not conform to the thermodynamic condition of reversibility implied in eqn. (1).

It is possible by considering the properties of suitable models to suggest how to obtain approximate solutions for such problems as these in the case that the adsorbed films are mobile and insoluble. Although this qualification necessarily limits the generality of the conclusions, mobile films are of common occurrence.[2] [3] [4] [5] The reason why it is possible to progress with such problems when the surface films are mobile is because a mobile film exerts a spreading pressure φ numerically equal to F. It is the action of the spreading force of the film on the underlying solid which causes the swelling so that observation of the changes in dimensions and the changes in mechanical properties which accompany adsorption provides additional evidence which may facilitate the interpretation of the adsorption isotherms.

A few examples as illustrations of one method of approach are given below. The earlier are concerned with the interaction between deformable solids and surface films and the later examples consider the additional effects arising from capillary condensation.

The Cause of Swelling by Adsorption of an Insoluble Mobile Film.—There are two recognised ways [6] [7] whereby a mobile insoluble film may cause a non-rigid adsorbent to swell. They correspond to the two cases mentioned earlier of swelling of the actual solid substance and swelling by separation of the constituent units.

If any system free from external restraint is in equilibrium, the net force acting across any imaginary surface dividing the system into two parts is zero. Then, if the system in equilibrium consists of a solid on which is adsorbed a mobile film, which exerts a spreading force, it follows that the solid must be in tension. Therefore, during the process of adsorption, the solid expanded. The second swelling mechanism corresponds to the earlier stages of a process of peptisation. If the fine-structured solid contains crevices too narrow to accommodate on either face an adsorbed film of the thickness natural to an external surface, the spreading force—squeezing the adsorbed phase into the crevices—will tend to force the walls apart.

Capillary Condensation.—When capillary condensation occurs, the surface becomes covered with liquid. The spreading pressure at the adsorbent-adsorbate interface then becomes, by the equation of Young and Dupre,[8] *

$$\varphi_{sl} = \varphi_{sv} + \gamma_{lv} \cos \theta$$

where φ_{sl} = spreading pressure when the surface is covered by liquid,
φ_{sv} = spreading pressure when the surface is covered by vapour,
γ_{lv} = surface tension of the liquid and
θ = contact angle.

Beyond the range of the surface field the liquid is under a tension, the magnitude of which, for a definite temperature, depends on the vapour pressure. Therefore when liquid condenses in a porous solid two new forces act, one parallel to the surface (due to the quantity $\gamma \cos \theta$[*]) and the other due to the hydrostatic tension in the liquid acting normally to the surface.

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[2] Bangham and Fakhoury, *J. Chem. Soc.*, 1931, 1324; Bangham, Fakhoury and Mohamed, *Proc. Roy. Soc. A*, 1934, **147**, 152.

[3] Gregg, *J. Chem. Soc.*, 1942, 696.

[4] Harkins and Jura, *J. Amer. Chem. Soc.*, 1944, **66**, 1356.

[5] Hill, *J. Chem. Physics*, 1946, **14**, 441.

[6] Bangham and Fakhoury, *Proc. Roy. Soc. A*, 1931, **130**, 81; Bangham, *Ultra-Fine Structure of Coals and Cokes* (B.C.U.R.A., 1944), p. 27.

[7] Orowan, *Nature*, 1944, **154**, 341.

[8] Bangham and Razouk, *Trans. Faraday Soc.*, 1937, **33**, 1459.

* Here φ is a positive and γ is a positive quantity so that, for $\theta < \frac{\pi}{2}$, φ_{sl} is greater than φ_{sv}.

For simplicity of calculation in those of the following examples which deal with capillary condensation, it will be supposed that the range of the surface field is negligible as compared with the distance of separation of the surfaces between which liquid condenses, and that, beyond this range, the liquid is under uniform tension.

(A) Adsorption without Capillary Condensation

I. Swelling by Stretching the Structural Units.—To show more clearly how to obtain the fraction of the free energy change of the solid which is stored as work of expansion, the model offering the simplest mathematical treatment is chosen.

Consider a cylindrical cavity of original length l_0 and radius r_0 with elastic walls (Fig. 1 *a*). The elasticity is supposed to be anisotropic so that the walls may stretch longitudinally but not radially. A small opening in one end of the cylinder allows the inner surface to adsorb vapour from the outside space.

On adsorption of a vapour the spreading force of the film acting on the ends of the cavity will extend the walls to a length l at which the elastic restoring force of the walls equals the spreading force of the adsorbed film. At equilibrium, for a solid obeying Hooke's law,

$$\varphi_l = k\,\frac{(l - l_0)}{l_0}$$

where k is a constant related to the elastic properties of the material. Then, for an expansion Δl

$$\begin{aligned}
\text{The work of expansion} &= 2\pi r_0 \int_{l=l_0}^{l=l_0+\Delta l} k\,\frac{(l - l_0)}{l_0}\,\mathrm{d}l \\
&= \tfrac{1}{2}\varphi_{(l_0+\Delta l)} \cdot (2\pi r_0 \,.\, \Delta l) \\
\text{The surface energy lowering} &= \varphi_{(l_0+\Delta l)} \cdot (2\pi r_0)\,(l_0 + \Delta l) \\
\text{The free energy lowering of the system} &= \varphi_{(l_0+\Delta l)} \cdot (2\pi r_0)\{(l_0 + \Delta l) - (\tfrac{1}{2}\Delta l)\}
\end{aligned}$$

$$\text{Hence the work of expansion} = \frac{\Delta l}{2l_0 + \Delta l} \cdot \{\text{Free energy lowering of the system}\}$$

$$\text{Using eqn. (1), work of expansion per unit mass of adsorbent} = \frac{\Delta l}{2l_0 + \Delta l} \cdot \frac{RT}{M} \int_0^p \frac{m_B}{m_A}\,\mathrm{d}\log_e f$$

This quantity may be evaluated experimentally.

Similar calculations may be made for more complicated models, e.g., for three-dimensional swelling of a cylindrical cavity, for the swelling of an assembly of spherical particles, etc. The consideration of other models will lead to a change in the proportionality factor which in the example above is $\Delta l / 2l_0 + \Delta l$.

II. The Widening of Crevices.—Structures such as those in Fig. 1 *d* and *e* may conveniently be represented by the model of Fig. 1 *g* and *h*, in which the resistance of the material at the head of a crevice to the spreading force which is tending to force the walls apart is represented as an elastic restraint controlling the distance of separation of rigid surfaces. Then, if the area of the rigid surface is A_1, and of the elastic material A_2, relations such as those developed in the preceding example will apply to the area A_2 only. It is unlikely that in any practical case the structure would be sufficiently well represented by the model for the ratio A_1/A_2 to have much significance, and the equations for the model are not developed.

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[*] It should be noted that the quantity $\gamma \cos \theta$ may depend on the vapour pressure at which condensation occurs.

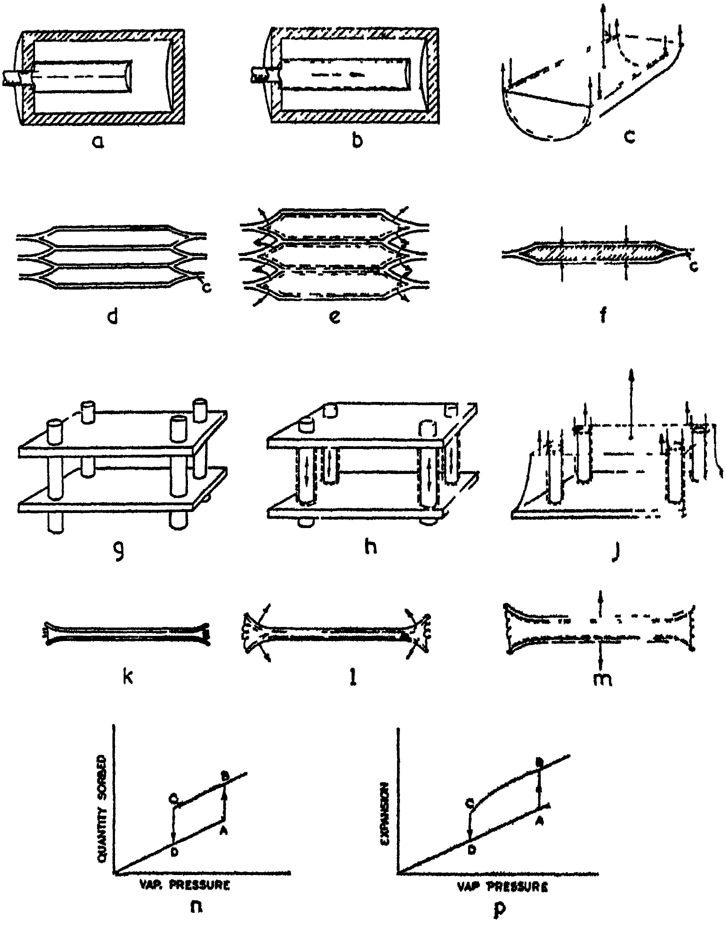

Fig 1.

Its important qualitative features are:

(1) the expansion is proportional to the spreading pressure φ,

(2) the work of expansion is smaller than in I by a factor depending on the ratio A_1/A_2. There is no limit to this ratio and the work of expanding the solid may be negligible.

III. Rigid Surfaces held together by Surface Forces with some Elastic Restraint.—If there are regions within a swelling solid where the surfaces are sufficiently close together for surface forces to contribute appreciably to the cohesion of the solid, the adsorption isotherm may be expected to show hysteresis. This is because surface forces decrease as an inverse power of the distance of separation so that a spreading force which just suffices to cause the surfaces to move apart will be more than sufficient to keep them apart.

A simple representation of such a system is shown in Fig. 1 *k, l, m*. An elastic restraint is incorporated to prevent infinite separation of the surfaces and it will be supposed that the solid may deform elastically around the cohering regions before these spring apart.

The characteristic features of the model would then be :

(1) in the early stages of adsorption, the expansion being controlled by elastic restraints would be proportional to the spreading pressure ;

(2) when the surfaces separate, the expansion and adsorption suddenly increase for constant spreading pressure ;

(3) after separation, the swelling being again limited by the elastic restraint is roughly proportional to the spreading pressure ;

(4) during desorption, the shrinkage is initially roughly proportional to the decrease in spreading pressure ;

(5) when the combined action of the surface forces and elastic restraint overcome the expanding action of the film there is a sudden collapse of the separated surfaces ; and

(6) in the final stage the shrinkage is proportional to the reduction in spreading pressure.

The behaviour of such a system is shown diagrammatically in Fig. 1 *n* and *p*.

It is also to be expected that the system would be more compressible after the originally cohering regions have been forced apart.

Since, along the path AB, Fig. 1 *p*, the expanding force exceeds the resistance to expansion and, along CD, the force of contraction exceeds the resistance of the film, neither the application of eqn. (1) to the adsorption isotherm nor to the desorption isotherm gives the free energy lowering of the system when exposed to saturated vapour. The former path would lead to a value too small and the latter to too large a value. There need be no relation between the area of the hysteresis loop observed experimentally and the mechanical work stored in the solid along the path AB, for it might happen that the sudden swelling enabled adsorbed vapour molecules to reach parts of the internal surface which they could not previously approach. The primary meaning of the hysteresis loop is that there is a barrier preventing the adsorption from continuing until the porous solid possesses the minimum free energy consistent with the vapour pressure.

It will be noted that in the important practical case for which the work of expansion is a small part of the free energy change due to adsorption, the application of the integrated Gibbs-Duhem equation to the *desorption* isotherm gives an approximate value for the surface free energy lowering of the system.

(B) Capillary Condensation

IV. Condensation in a Cylindrical Cavity with Thin Walls of Isotropic Material.—(*a*) The author has shown elsewhere[9] that when capillary condensation takes place in a cylindrical cavity with thin isotropic walls, the tube shrinks radially. The new radius r is given by

$$\frac{\gamma \cos \theta}{\varphi} = \frac{r_1}{r_1 - r_0} \cdot \frac{r_1 - r}{2r - r_1}$$

where r_0 is the original radius *in vacuo*, and r_1 is the radius when the capillary is expanded by the film pressure φ. As a result of the radial shrinkage, when the vapour pressure is lowered slightly, liquid will remain in the tube, i.e., the adsorption isotherm exhibits hysteresis.

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[9] Hirst, *Nature*, 1947, 159, 267.

(*b*) The decrease in the longitudinal expansive force is

$$\frac{2\pi(r_1 - r)}{r_1}\left\{r_1\varphi - r\gamma\cos\theta\right\}$$

so that the length of the cavity will decrease, remain constant, or increase according as $r_1\varphi$ is greater than, equal to, or less than $r\gamma\cos\theta$. Since r_1 is necessarily greater than r and since at saturation pressure φ for many adsorbent-adsorbate systems is several times as large as $\gamma\cos\theta$, it is to be expected that on capillary condensation at higher vapour pressures a longitudinal *contraction* would occur.

On raising the vapour pressure further, the tension in the condensed liquid relaxes and it is under no tension when in equilibrium with the saturated vapour. The swelling pressure at the solid-liquid interface is then equal to the sum of the pressure in a surface film when exposed to saturated vapour and the quantity $\gamma\cos\theta$.* It is, therefore, the same as it would have been had the porous solid been completely immersed in liquid and there would be no change in dimensions if this were done.

It will be noted that as a consequence of condensation the radial expansion (and probably the longitudinal expansion also) would increase more rapidly with pressure than it would if condensation did not occur.

V. Condensation between Plane Parallel Rigid Surfaces held by Restraints.

If A is the free area of the rigid plates (Fig. 1 *h*),
d is their distance of separation,
L is the periphery of the plates,
l is the total periphery of the restraints, and
a is the cross-section of the restraints.

On condensation, the force tending to cause contraction

$$= \frac{2\gamma\cos\theta . A}{d} + \gamma\cos\theta . L$$

and the force opposing contraction $= l(\varphi + \gamma\cos\theta) + a$ (some function of the mechanical properties of the restraints).

If the mechanical properties of the restraining material are known, the dimensional changes accompanying condensation can be calculated. The important distinction between this and IV is that the ratio of the magnitudes of the force of contraction to the opposing force may have any value and a sufficiently slight restraint would be completely overcome on condensation of liquid and the system collapse. It will be noted that should the actual structure of the system be similar to that depicted in Fig. 1 *d*, the contact areas such as are marked C in Fig. 1 *d* and *f* may increase after condensation and the mechanical compressibility of the system decrease. The isotherm would exhibit hysteresis for the same reason as in IV *a*.

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* Note, as before, that this quantity may not be constant but depend on the vapour pressure.

Conclusions

The usefulness of these examples is most simply illustrated by the following conclusions which may be drawn from them.

1. If it is possible to estimate the work of expanding a solid from independent measurements of its mechanical properties, calculations such as those in I may determine whether swelling is due to an extension of the actual substance of the solid or represents a separation of the constituent units (I and II).
2. The interplay between the spreading force of the adsorbed film and the elastic restraints of the solid system may control the magnitude of the swelling even though the work of expansion is negligible (II).
3. If the isotherm exhibits hysteresis due to the mechanism of III and the work of expansion is small, the *desorption* isotherm may be used to obtain an approximate figure for the free energy lowering of the system.
4. If the hysteresis in an isotherm is due to the mechanism of III, measurements of the length and deformability of the system over the region of hysteresis would show that on desorption the system would be larger, and more deformable than on adsorption.
5. If liquid condenses in capillaries of uniform size in a solid, the latter should shrink radially (IV). In practice, the capillaries in a solid would probably cover a range of sizes and the effect due to capillaries within a given narrow range of diameters might be masked by the relatively rapid expansion of other capillaries after condensation.
6. On capillary condensation in a system such as shown in Fig. 1 *d* its deformability might decrease. But, again, this effect would probably not be observed in practice for reasons analogous to those given in 5 above.
7. If there is capillary condensation and the system be in equilibrium with the saturated vapour, no change in length would be observed on plunging the system into liquid (IV *c*). Conversely, should a change in length be observed, capillary condensation has not occurred. This argument was first advanced by Bangham.[10]
8. If condensation occurs between parallel plates whose distance of separation is controlled by only weak constraints, the system may collapse.

In conclusion, it is desirable to mention that the two mechanisms described above which would lead to hysteresis in the isotherms of vapours on swelling fine-structured solids are not the only causes of hysteresis but are additional to a number of other causes, notably hysteresis due to phase transitions in the adsorbed films,[3] which have been discussed by other authors. The dominant point brought out by consideration of the models is that although swelling complicates the adsorption phenomena, a study of it and of the mechanical properties of the swelling solid may provide the evidence necessary to solve the additional problems presented.

This work is part of a fundamental investigation of the influence of moisture films on the strength and breakage of coals and of the influence of sorption swelling on the movement of assemblies of fuel particles.

Summary

The adsorption isotherms on swelling solids are more difficult to interpret than those on rigid materials. However, if the adsorbate is insoluble and forms mobile-surface films, the swelling is caused by the spreading force of the film acting on the underlying solid. Observation of the changes in dimensions and mechanical properties which accompany adsorption therefore provides evidence to help in interpreting the adsorption isotherms. Suggestions are offered as to how this may be done for a number of simple models.

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[10] Bangham and Razouk, *Proc. Roy. Soc. A*, 1938, **166**, 572.

SOME PROPERTIES OF WATER ADSORBED IN THE CAPILLARY STRUCTURE OF COAL

BY R. L. BOND, M. GRIFFITH AND F. A. P. MAGGS

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The examination of the properties of adsorbed water is of importance since water is present to a considerable extent in many naturally occurring materials used in industry; for instance, a quantity of water of the order of millions of tons is mined annually in association with coal in this country. Much interest lies, then, in the *attributes* of the adsorbed phase, and, since it is often implicit in publications dealing with the gas-solid interface that water adsorbed on porous solids simulates the behaviour of bulk water, this paper describes a few critical experiments designed to emphasise any differences that may exist between the two phases.

The numerous applications of the theory of capillary condensation [1] have a common basis in the assumption that vapours adsorbed on any fine-structured solid will be in equilibrium with a vapour pressure uniquely determined by the curvature of the meniscus formed in the micro-capillaries, even if these are of molecular dimensions; hysteresis is ascribed to a change in the angle of contact between this meniscus and the solid (or film-covered solid).* Whilst identity between bulk liquid and the adsorbed film formed at saturation is not explicitly postulated by Brunauer, Emmett and Teller [2] in their multilayer theory, it is difficult to resist the conclusion that infinite adsorption of bulk liquid on plane surfaces is implied. Again, Harkins,[3] in his calorimetric method of estimating surface areas, assumes that an adsorbed film of water on anatase at saturation vapour pressure possesses a surface energy identical with that of the free liquid.

In contrast with these assumptions we may recall Foster's [5] observation that no sign of condensation of water on silica gel—a system regarded as a classical example of capillary condensation—could be detected very close to saturation, even though the isotherm took a sharp upward turn at high relative pressures. Similarly, Bangham [6] observed that drops of liquid placed on the surface of mica subjected to a jet of the supersaturated vapours refused to spread. He also measured a free-energy change, not equal to but less than the surface tension of the liquid, on immersing in liquid methanol and ethanol rods of charcoal previously saturated from the vapour phase. Bangham [24] concluded that a difference of phase exists between the adsorbed film and bulk liquid. (See also Frumkin [7] and Cassel.[8]) Indeed, Gregg and Maggs [9] find that many apparent examples of capillary condensation are more fittingly attributed to changes of phase *within* the adsorbed film.

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[1] Zsigmondy, *Z. anorg. Chem.*, 1911, **71**, 356.
[2] Brunauer, Emmett and Teller, *J. Amer. Chem. Soc.*, 1938, **60**, 309.
[3] Harkins and Jura, *J. Amer. Chem. Soc.*, 1944, **66**, 1362.
[4] Hirst, *Nature*, 1947, **159**, 267.
[5] Lambert and Foster, *Proc. Roy. Soc. A*, 1932, **134**, 246.
[6] Bangham and Saweris, *Trans. Faraday Soc.*, 1938, **34**, 554.

* From a different standpoint, Hirst [4] has shown that hysteresis is a possible consequence of the effect of changed pore dimensions brought about by liquid condensation.

The pore structure of coal is particularly favourable to the occurrence of capillary condensation; density measurements made by Franklin[10] have shown that the pores contain constrictions of molecular dimensions, the size of the constrictions decreasing with increasing maturity of the coals. We shall show, however, that although the observations, particularly at saturation vapour pressure, point to the occurrence of liquid condensation, certain aspects of the behaviour of the adsorbed and the bulk water stand in very sharp contrast. That these divergencies in behaviour represent a real phase difference is amply demonstrated by the qualitative experiments to be described; a quantitative examination of the phenomena is in hand.

Experimental

Samples.—The coals used in this work were stored in nitrogen as $\frac{1}{4}''$ slack; a sample of each coal was withdrawn, ground to pass 72 B.S.S. and kept in sealed bottles until required. For experiments using — 240 B.S.S. coal, samples were taken from these bottles and ground by hand. The analyses of the coals (— 72 B.S.S.) are given in Table I.

We shall have occasion whilst discussing the results to refer to the porosity and surface area of the coals. By porosity is meant the volume of the pores which is accessible to helium in a *lump* of coal; the porosity values quoted here are those given by Franklin,[10] whose coal samples were taken from the same batch as those used in the present work. Values for the inner surface area of coals are calculated directly from the heat of wetting of the coal in methanol.[11]

In all the tables, coals are arranged in order of decreasing rank.

TABLE I

ANALYSES OF COALS USED

Coal		Proximate Analysis (air-dried basis)					Ultimate Analysis d.m.f. (Parr's basis)				Heat of Wetting in Methanol* cal. g.$^{-1}$
Description (Seyler's Classification)	Locality	Volatile Matter %	Moisture %	Ash %	Fixed Carbon %	Volatile Matter d.m.f. %	Carbon %	Hydrogen %	Oxygen %	Nitrogen %	
C. Anthracite, Group A1	S. Wales	4·7	2·6	2·1	90·6	4·9	94·2	2·9	1·7	1·2	8·5
D. Carbonaceous ..	S. Wales	14·8	1·1	2·5	81·6	15·2	91·7	4·4	2·4	1·5	4·6
F. Meta-bituminous ..	S. Wales	23·3	1·4	4·4	70·9	24·0	89·4	4·8	4·1	1·7	4·8
H. Para-bituminous Meta-lignitous ..	Yorkshire	32·5	6·1	1·6	59·8	35·2	83·1	5·1	9·9	1·9	12·9
K. Meta-lignitous ..	Northumberland	33·8	10·4	0·9	54·9	37·9	82·6	5·3	10·1	2·0	17·6

* Samples were ground to pass 240 B.S.S.

A. Porosity and the Volume of Water Adsorbed at Saturation.—Samples of the coals, ground to pass 240 B.S.S., contained in tared weighing bottles, were thoroughly evacuated; dry air was then admitted and the stoppered bottles were immediately weighed. After further evacuation the coals were exposed to saturated water vapour until adsorption ceased, the

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[7] Frumkin, Gogoritzkaja, Kabanov and Nekrassov, *Physik. Z. Sowjet.*, 1932, **1**, 255.

[8] Cassel, *J. Chem. Physics*, 1945, **13**, 249.

[9] Gregg and Maggs, *Trans. Faraday Soc.*, 1948, **44**, 123.

[10] Franklin, *Ph.D. Thesis* (Cambridge, 1946).

[11] Maggs, *Proc. Conf. Ultrafine Structure of Coals and Cokes* (B.C.U.R.A.), 1944, p. 95; Bond and Maggs, *Coal Research* (in press).

adsorbed water being measured by reweighing. The results are recorded in column 3 of Table II. (Good agreement with these values was also given by exposing the same coals to saturated water vapour in a desiccator evacuated on a filter-pump, although somewhat longer times of exposure were required.)

TABLE II

ADSORPTION OF WATER AT SATURATION VAPOUR PRESSURE ON COALS

Coal	Porosity 10^{-2} cc./cc.	Saturation Adsorption 10^{-2} g./g.	Saturation Adsorption 10^{-2} cc./cc.
C	10·1	5·9	8·9
D	2·2	1·7	2·2
F	3·2	3·6	4·7
H	7·7	10·0	13·0
K	12·3	12·1	15·7

A comparison of the saturation adsorption—expressed in cm.^{3} water adsorbed per cm.^{3} of dry coal—with the porosity of the coal reveals that with some of the coals more water is adsorbed than would be required merely to fill the pores. Some light is thrown on this by the following experiment (suggested by previous work with methanol [12]). A prism of coal K was evacuated, weighed and its size measured with a dial gauge; re-evacuation was followed by the adsorption of saturated water vapour; the swelling and the quantity of water adsorbed were measured, with the results shown in Table III. (V, S and P represent the volume of wate· adsorbed, the volume swelling and the porosity, respectively, and are expressed in % by volume.) Three experiments were made on the same prism.

TABLE III

SWELLING OF COAL K IN WATER VAPOUR

% Weight Adsorbed	V	S	P
9·9	13·1	2·4	11
10·2	13·6	2·0	11
9·5	12·6	2·1	11

The volume adsorbed is equal quantitatively to the sum of the volume swelling and the porosity and there is thus *prima facie* evidence that the pore volume of the swollen coal is completely filled with adsorbed water at saturation.*

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[12] Maggs, *Trans. Faraday Soc.*, 1946, 42B.

* In the experiments with methanol, a surface compression was measured as a reduction in the total volume of the system; this effect appears to be small in the present case.

King and Wilkins [18] have assumed the volume of water adsorbed at saturation vapour pressure to be equal to the porosity of the coal. Of the liquids of small molecular volume able to penetrate the coal structure, water is the most suitable both on account of the negligible adsorption compression * and the relatively small swelling (coal K swells about 16, 9 and 2 % by volume in methanol, benzene and water respectively). With low-rank bituminous coals, however, neglect of the adsorption swelling is liable to introduce errors up to 3 % in the porosity; with lignites the error is probably considerable (a volume swelling of 25 % has been observed by us on immersing a lignite in water).

B. Adsorption Isotherms.—Since coals are often exposed to air of various humidities the form of the adsorption isotherm is of importance practically; at the same time, the deductions to be drawn from such data add considerably to our knowledge of the nature of the adsorbed water.

APPARATUS.—A conventional volumetric apparatus was slightly modified (Fig. 1) to facilitate measurement of the adsorption up to saturation vapour pressure. The manometer (A) was of 20 mm. tubing to avoid meniscus errors. Distilled water (bulb B) was further purified by fractional distillation under vacuum in the apparatus. The burette (C) (*ca.* 620 cc. capacity) and the sample bulb (D) were situated in a water-bath kept at 24·56 ± 0·02° C. In general, a measured quantity of water vapour was frozen into appendix E from the burette, cut-off F was raised and on lowering cut-off G and warming the appendix, adsorption took place. The vapour pressure in the burette was never allowed to rise above 0·8 saturation vapour pressure, so that deviations from the gas laws were minimised. For pressures greater than this, and approaching saturation V.P., equilibrium was established between the coal and liquid water in the appendix H, the quantity not adsorbed being

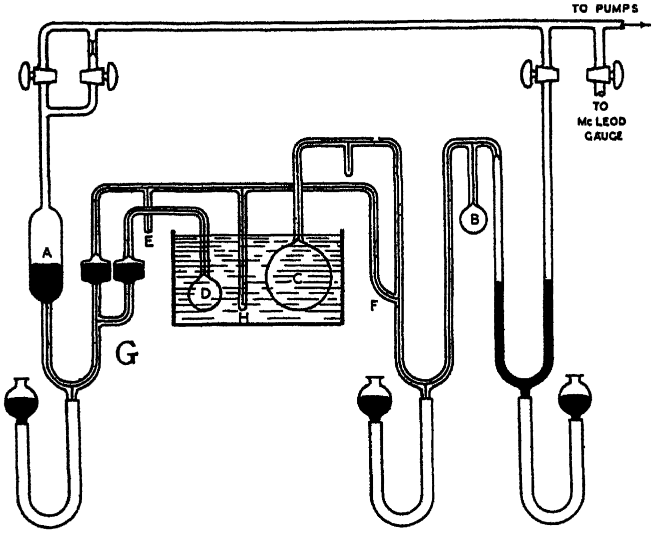

FIG. 1.—Volumetric adsorption apparatus.

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[18] King and Wilkins, *Proc. Conf. Ultrafine Structure of Coals and Cokes* (B.C.U.R.A.), 1944, p. 46.

* Adsorbed methanol, for instance, occupies 17 % less volume than does free liquid methanol.[18]

measured in the burette; this appendix was immersed in the water-bath. The coals were prepared by grinding through 240 B.S.S. as this has been found to lead to speedier adsorption than with coarser material. A blank experiment was performed to test the behaviour of the apparatus, especially in view of an observation by Norrish[14] of marked adsorption of water on the glass apparatus. The magnitude of the experimental error (whether due to adsorption on the glass, errors of measurement or deviation of water vapour from the gas laws) is shown to be small by the result of the blank experiment (curve (*a*), Fig. 2).

The isotherms are given graphically in Fig. 2. The saturation values obtained in Section A have been included in Fig. 2 and the adsorption branches extend to these. The isotherms given by coals H and K are similar to those found for systems where bulk condensation is said to occur; moreover, the decrease in hysteresis as the coals increase in rank could be readily related to the concomitant reduction in the size of the pores.

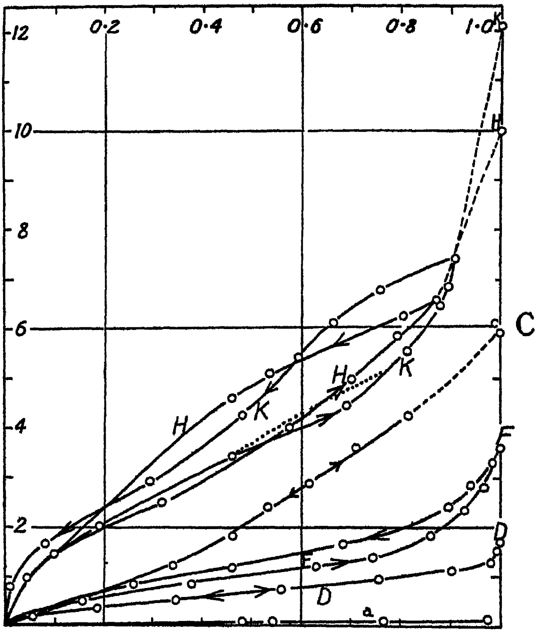

FIG. 2.—Adsorption isotherms of water on five coals at 25° C.
Ordinates: Percentage weight adsorbed.
Abscissæ: Relative pressure.

If we suppose for the moment that the adsorbed film does not differ from bulk water, several properties of the adsorbate may be readily measured. Whilst values of the vapour pressure and freezing point, for instance, may be susceptible to the influence of the pore diameter, measurement of the dielectric constant and of the volume change on freezing would provide critical data for testing the initial postulate. Such measurements are described in sections C and D.

C. Freezing Point of Adsorbed Water.—A characteristic property which could be used for identifying bulk water is the sharp volume change which occurs on freezing. The volume of water adsorbed by certain bituminous coals (e.g., coal K) is sufficiently great to cause a volume change at the freezing point, which could be readily detected dilatometrically if it occurs and is of the same magnitude as that of bulk water.

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[14] Norrish and Russell, *Nature*, 1947, 160, 57.

From saturated vapour 12 % by weight of water was adsorbed at 21° C. by a sample of coal K ground to pass 72 B.S.S. This saturated coal sample was put into a thin-walled glass cylinder to which a calibrated capillary tube was attached; the system was then completely filled with water-saturated dibutyl phthalate.* The temperature of this system was decreased steadily from that of the room to about — 70° C., and changes in volume of the coal and adsorbed water were detected by the movement of the meniscus in the capillary tube. To correct for extraneous volume changes due to components of the system other than adsorbed water, control dilatometers were used, making a total of seven, filled as follows:

(1) Dry dibutyl phthalate.
(2) Dibutyl phthalate saturated with water.
(3) Dry coal (—72 B.S.S.) + dry dibutyl phthalate.
(4) Dry coal ($\frac{1}{8}$") + dry dibutyl phthalate.
(5) Dibutyl phthalate + 1·5 cm.^{3} liquid water.
(6) Coal (—72 B.S.S.) saturated with water vapour + dibutyl phthalate saturated with water + 0·5 cm.^{3} liquid water.
(7) Coal (—72 B.S.S.) saturated with water vapour + dibutyl phthalate saturated with water.

The readings of the meniscus levels in the capillary tubes are plotted against temperature in Fig. 3; the ordinate units are arbitrary.

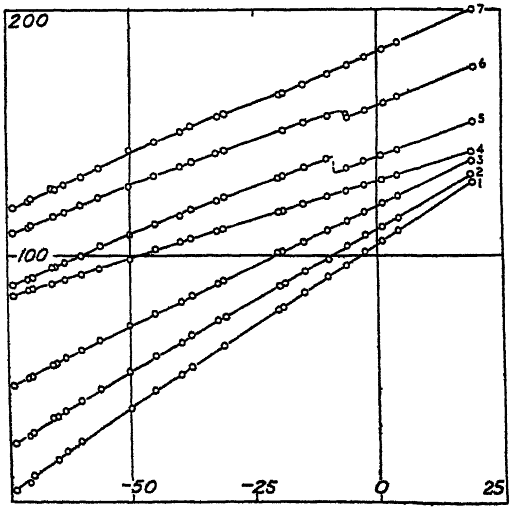

FIG. 3.—Dilatometric experiments.

Curve 1. Dibutyl phthalate, dry.
2. Dibutyl phthalate, saturated with water.
3. Dry coal (— 72 B.S.S.) + dry dibutyl phthalate.
4. Dry coal ($\frac{1}{8}$" pieces) + dry dibutyl phthalate.
5. Saturated dibutyl phthalate + 1·5 cm.^{3} water.
6. Coal (— 72 B.S.S.) saturated with water vapour + 0·5 cm.^{3} excess water and saturated dibutyl phthalate.
7. Coal (— 72 B.S.S.) saturated with water vapour + saturated dibutyl phthalate.

Ordinates: Scale readings of menisci (in cm.).
Abscissæ: Temperature ° C.

The blank experiments of bulbs (1) and (2) show that no correction need be applied for unusual volume changes in the dilatometric liquid. The experiment with bulb (5) (containing water and dibutyl phthalate) shows that the presence of the oil-water interface will not prevent freezing; that is, the experimental conditions were suitable for the detection of bulk water.

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* It was anticipated that the very large molecules of this liquid would be unlikely to penetrate the pore constrictions of the fine structure of the coal and displace the adsorbed water molecules. Dibutyl phthalate has the further advantage of being deformable even at — 70° C. and was therefore suitable for use as a dilatometric fluid in this series of experiments.

The volume change of the bulk water is marked (bulb 5); its occurrence at about — 8° c. appears to be due to supercooling.*

The quantity of water adsorbed in the coal was similar to that in the bulb (5); freezing of the adsorbed water could therefore be readily detected. It is clear from curve 7 in Fig. 3 that a phase change of this nature *does not occur* between + 20° c. and — 70° c. for adsorbed water. Whilst precautions were taken to keep the coal saturated with water (e.g. the dibutyl phthalate was water-saturated before the experiment), the theory of capillary condensation assumes that the pores will contain bulk liquid over a range of relative pressure, particularly in the steeply rising final part of the isotherm[15]; therefore, failure to detect a freezing point cannot be ascribed to this cause. In the case where water in excess of that required for saturation of the coal was present (bulb 6), a volume change corresponding to that caused by the freezing of the *excess* water alone was observed; even the ice thus formed failed to crystallise the adsorbed water. Such an experiment provides a simple method of determining the quantity of ordinary water present in coal.

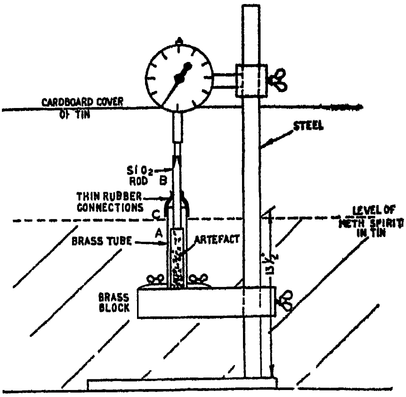

Fig. 4.—Thermal expansion apparatus.

Some degree of supercooling is easily attained, and it might be thought that in small pores where disturbances (such as convection currents) are minimised, considerable supercooling would be possible. It has been shown, however, that the presence of coal is sufficient to crystallise supercooled bulk liquid (footnote, p. 35 also curve 6, Fig. 3). It seems most improbable that the absence of freezing of the adsorbed water at so low a temperature as — 70° c. can be attributed to ordinary supercooling.

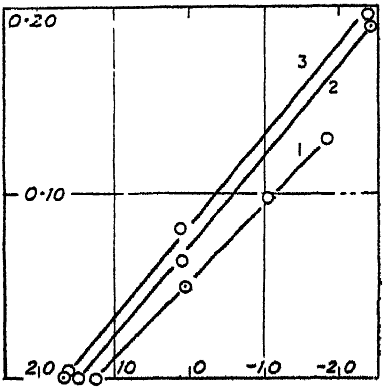

Fig. 5.—Thermal expansion of coal K containing adsorbed water.
Curve 1. Dry coal.
2. Coal + 3·7 % adsorbed water.
3. Coal + 14·2 % adsorbed water.
Ordinates: Percentage-contraction.
Abscissæ: Temperature ° c.

Some supporting experiments have been made in which the coefficient of thermal expansion of coal K (in the form of rods of compressed powder) was measured between + 20° c. and — 20° c., using the apparatus shown in Fig. 4. Measurements were made on rods of the compressed coal powder, both dry and with adsorbed water. Blank experiments using silica rods of negligible thermal expansion were used to correct for length changes of the apparatus. The results are shown in Fig. 5, where the percentage change in length is plotted against the temperature. Again, the results gave no indication of freezing of the water in this temperature range. It was observed, however, that the coefficient of thermal expansion was changed from $4{\cdot}2$ to $5{\cdot}0 \times 10^{-5}\,^{\circ}\,\text{C.}^{-1}$ by the adsorption of water at saturation V.P.

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[15] Cohan, *J. Amer. Chem. Soc.*, 1938, **60**, 433.

* Water cooled in glass tubing remained liquid at — 10·5° c.; no special precautions were needed to achieve this. Vibration or tapping did not induce crystallisation, but a thin glass rod or a speck of coal (either dry or wet) immersed in the supercooled water caused freezing.

D. Dielectric Constant.—In another method employed for investigating the behaviour of adsorbed water advantage was taken of the fact that, at an appropriate frequency, a marked change in dielectric constant occurs when water freezes. The temperature dependence of the capacitance of a condenser containing saturated coal was measured at a frequency of 15 kc./sec. using a high-frequency bridge of the Schering type fitted with a Wagner earth; balance points were located with a Muirhead amplifier detector. A substitution method was employed, the capacitance under investigation being in parallel with an N.P.L.-calibrated, variable air condenser.

Three sets of data were obtained with the same parallel plate condenser, supported in a bath which could be held at any required temperature between + 20° and − 70° C. Determinations were made of the capacitance of the condenser with the following materials forming its dielectric: (1) air, (2) dry coal K, ground to pass 72 B.S.S., and (3) the same coal saturated with water vapour at 25° C. The possibility of very slow heat transfer was investigated and rejected, and readings were taken only after both temperature and capacitance readings had remained steady for 30 min. An apparent dielectric constant ε' was measured, which represents the dielectric constant of the coal powder plus voidage; such comparative values are adequate for the detection of the liquid-solid phase change. The variation of ε' with temperature for the three systems is given in Fig. 6. Curve (1) shows that corrections for the variation of the capacitance of the empty condenser with temperature are negligible.

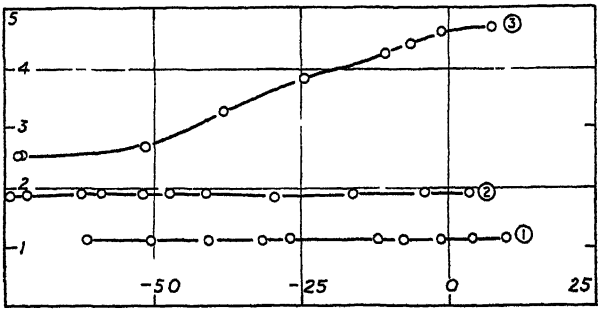

FIG. 6.—Dielectric constant of coal K containing adsorbed water.
Curve 1. Air.
2. Dry coal.
3. Coal saturated with water vapour.
Ordinates: Apparent dielectric constant.
Abscissæ: Temperature ° C.

The effect of the adsorbed water on ε' for coal is very marked and is greater than would be anticipated for the addition of 12 % bulk water.* The dispersion curve for the system coal plus adsorbed water shows no break which might denote freezing (such as those found for clays [16]). On the other hand, the occurrence of partial freezing at successively lower temperatures is not precluded.

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[16] Alexander and Shaw, *J. Physic. Chem.*, 1937, **41**, 955.

* From Wiener's law (random distribution of spheres), or from work of Sillars, *J. Inst. Elect. Eng.*, 1937, **80**, 378.

E. Wetting and Free-Energy Changes at Coal Surfaces.—The measurement of the free-energy changes which take place on immersing coal, saturated from the vapour phase, in water provides a reliable method for the detection of phase differences. Whilst the free-energy decrement during adsorption from the vapour may be easily evaluated from the adsorption isotherm, that which occurs on immersion is less readily evaluated. For charcoal rods, however, Bangham[17] has shown that the adsorption expansion is directly proportional to the free-energy change, and this observation provides a method for overcoming the difficulty in dealing with immersion.

(*a*) ENERGY CHANGE ON ADSORPTION FROM THE VAPOUR.—The free-energy decrements (F_s) at saturation vapour pressure have been evaluated from the isotherms of Fig. 2 by the relation developed by Bangham[18]:

$F = \frac{RT}{M\Sigma}\int_0^{p_1} s\,d(\log_e p)$; s being the adsorption at the interface of extent Σ, at the vapour pressure p_1. By taking values for Σ from the heats of wetting in methanol, F_s has been estimated for the five coals ; the results of these calculations are given in Table IV.

TABLE IV

ENERGY CHANGES OCCURRING DURING ADSORPTION OF WATER VAPOUR

Coal	$F_s\Sigma$ (from adsorption) 10^7 erg. g.$^{-1}$	$F_s\Sigma$ (from desorption) 10^7 erg. g.$^{-1}$	F_s (from adsorption) erg cm.$^{-2}$	F_s (from desorption) erg cm.$^{-2}$
C	6·1	6·1	69	69
D	2·2	2·2	52	52
F	3·4	4·0	71	84
H	12·2	15·9	89	117
K	12·8	17·3	73	98

A feature of these results lies in the contrast with the values obtained for organic liquids on coals, the value of F_s for a saturated methanol film[11] being about 200 erg. cm.$^{-2}$. The surface pressure of a film of adsorbed water is evidently insufficient to displace adsorbed films of organic vapours from coal surfaces.

(*b*) ADSORPTION SWELLING.—The relation between the swelling and the energy change at various points of the isotherm has been tested in the following manner: A rod of coal K, formed by pressing the powder (—72 B.S.S.) at 3 ton in.$^{-2}$, was placed in a metal extensometer attached to a glass vacuum system by a copper-glass seal. The extensometer consisted of a dial gauge graduated in 10^{-3} cm. which was enclosed in a close-fitting metal jacket, provided with a plate-glass window. Since it was found that the metal of the extensometer also adsorbed water vapour, it was necessary to measure the adsorption on a further rod of compressed powder contained in a glass jacket attached to the system through a ground-glass joint. This jacket (which was fitted with a tap) could be detached and weighed at appropriate intervals. The whole apparatus was kept in an air thermostat held at 25° C. Thorough out-gassing of both coal and water preceded the experiment. The free-energy change at various adsorptions was estimated from the isotherm K of Fig. 2.

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[17] Bangham and Razouk, *Proc. Roy. Soc. A*, 1938, **166**, 572.

[18] Bangham and Fakhoury, *Proc. Roy. Soc. A*, 1931, **130**, 81; Bangham and Fakhoury, *J. Chem. Soc.*, 1931, 1324.

In Fig. 7 the results of this experiment are expressed as the variation of the percentage linear expansion with both the weight of water adsorbed and the free-energy change occurring on adsorption. Whilst in the former case the curve is not linear, proportionality is shown between the swelling and the energy change (curve 2, Fig. 7). By using the value of the gradient of the latter curve, it is possible to estimate free-energy changes from the accompanying expansion.

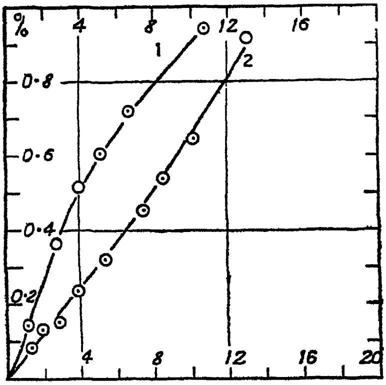

Fig. 7.—Adsorption expansion of coal.

Curve 1. Variation with weight adsorbed.

2. Variation with free-energy decrement.

Ordinates: Percentage linear expansion.

Abscissæ: Upper: Free energy decrement 10^7 erg $g.^{-1}$.

Lower: Percentage weight of water adsorbed.

(c) The Free-Energy Relation between Saturation and Immersion.—The free energies of saturation and immersion of plane surfaces are related in the following manner: $F_L = F_S + \gamma \cos \theta$, where γ is the surface tension of the liquid and θ is the angle of contact between the liquid and the vapour-saturated solid. Thus, the saturated solid will expand on immersion if $\theta<\frac{\pi}{2}$, and will contract if $\theta>\frac{\pi}{2}$. Identity between the liquid and adsorbed phases is, of course, shown by $\theta = 0$, when a marked increase in length will occur.

The rod of compressed coal used in the experiment of the previous section was mounted in the dial-gauge extensometer and, after thorough evacuation, was exposed to saturated water vapour at 25° C. for 3 days. A linear expansion of 1·23 % was recorded. Boiled distilled water was then admitted through a tap. The final expansion was 1·28 %. The angle of contact calculated from these results is 4° under $\frac{\pi}{2}$. In view of the closeness of this result to the critical angle of $\frac{\pi}{2}$, further experiments were devised which are based on the following considerations.

The significance of a finite angle of contact (as Bangham[24] has emphasised) is that it demonstrates the degree of incongruity between the surface of the bulk liquid and the adsorbed film on the solid, and one of the simplest ways in which the presence of a finite angle of contact can be shown for solids of density greater than that of the liquid is by flotation experiments. A zero angle of contact, for instance, leads to the inability of the solid to float at all, whilst for a powder which floats the value of θ must be finite. The ability of the solid to float is dependent on the shape of the solid as well as the angle of contact; a solid having vertical sides, however, will float above the surface only if $\theta > \frac{\pi}{2}$ according to the following relation:

$$g(V\rho_S - V_i\rho_L) + P\gamma\cos\theta = 0;$$

in which g = acceleration due to gravity; P = the periphery of the solid at the liquid meniscus; V = volume of solid, and V_i = the volume immersed. For systems where $\rho_S > \rho_L$ the solid will float above the surface *only when* $\theta > \frac{\pi}{2}$, *the depth of immersion being dependent on the ratio of* periphery to volume. The densities of the coals measured by helium displacement lie between 1·5 and 1·3 g. cm.$^{-3}$, and the lump densities of the dry coals fall in the range 1·37 to 1·15 g. cm.$^{-3}$. Calculation shows that the largest *cube* of coal which would just float (i.e., taking $\theta = \pi$) is a centimetre cube.

(*d*) FLOTATION EXPERIMENTS.—Samples of all five coals (ground to pass 72 B.S.S.) were sprinkled on clean water surfaces; none of the coals showed any tendency to sink, even after 20 weeks. To obviate any effects which might be attributed to adsorbed gases, the simple apparatus sketched in Fig. 8 was used. Coal powders were well evacuated at 80° C., allowed to reach equilibrium with saturated water vapour at room temperature and then tipped on to the water surface. Apart from a few particles (<1 %) which sank immediately, the saturated coal remained floating on the surface for the following ten weeks, after which observations were discontinued.

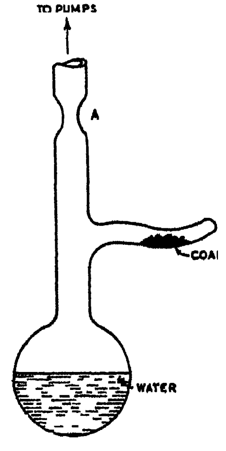

FIG. 8.—Apparatus for flotation experiments.

Adequate confirmation of the flotation experiments was obtained when flat plates of coal weighing up to 60 g. were easily floated by placing the coal on a freshly floated filter-paper, which sank leaving the coal afloat. A further experiment was made, in which the piece of coal was placed on thoroughly degassed ice. After several hours' pumping (with the water frozen) the ice was allowed to melt; the coal floated and had not sunk after 6 days.*

It was found impossible to fulfil the conditions of the flotation equation, for, whatever the size or shape of the lump, the unwetted upper surface of the coal lay below the plane of the water surface; in all cases the water meniscus curved downwards to meet the periphery of the upper surface of the lumps.

It is concluded from these experiments that the angle of contact between water and coal K is finite and is a little under $\frac{\pi}{2}$.

Preliminary quantitative experiments have been made by measuring the minimum load required to sink a number of pieces of coal; whilst the influence of the extent of the periphery is predominant, it is apparent that the evaluation of θ will involve the shape of the meniscus and the surface tension of the liquid. For instance, the action of wetting agents—which cause the coal lumps to sink—may depend on the reduction of θ, or the lowering of the surface tension, or—more probably—on both. Work is in hand to elucidate these points.

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* On pumping a piece of coal floating on *water*, bubbles of gas steadily escaped from the coal, which *remained floating*, until a large bubble from the water burst, so swamping the coal.

Nature of the Adsorbed Film of Water.

Interpretation of the results reported in Sections A and B along the lines of the B.E.T. multilayer theory or of the capillary condensation theory would lead to the conclusion that the water adsorbed by coal at saturation vapour pressure has the properties of three-dimensional liquid water. The critical experiments of the subsequent sections, however, make this simple conclusion untenable.

The proportionality between the adsorption expansion and the surface pressure of the water film at room temperature (Section E) leaves little doubt that the water-coal system behaves in the same manner as the charcoal-alcohol systems investigated by Bangham,[17] where the adsorbed films were shown to behave as a two-dimensional phase. It is at once apparent that the increase in the coefficient of thermal expansion of coal compacts brought about by adsorbed water is due to the kinetic mobility of the adsorbed molecules.

By regarding the two-dimensional film of water as a distinct phase, the absence of a normal melting-point is understandable.* It is not clear, however, whether a gradual transition to a solid phase takes place when the temperature is steadily lowered. Hardy,[20] for instance, found that the water in plant cells froze in stages, the proportion of ice formed being dependent on the lowering of the temperature. On the other hand, Foster [21] could find no evidence of the freezing of water adsorbed on silica gel even at − 65° c.; Rau [22] was able to supercool water droplets to − 72° c., but, as Bangham [23] has pointed out, there is some evidence to suggest that the water surface of drops at this temperature was remarkably akin to the adsorbed phase. From the several lines of approach described in this paper it is concluded that it is incorrect to treat adsorbed water as though it were bulk water.

The authors are glad to acknowledge the help and suggestions of Dr. D. H. Bangham, Director of Research Laboratories, British Coal Utilisation Research Association, in planning this work; they are grateful to the Council of the Association for permission to publish these results.

Summary.

The relation between liquid water and adsorbed water is discussed in the light of current theories, and whereas capillary condensed water might be expected to possess the properties of the bulk phase, measurements of the dielectric constant and volume changes on cooling coal saturated with water vapour show no evidence of a sharp freezing point. The significance of the angle of contact between liquid water and saturated coal is discussed; measurements of the free-energy decrement on wetting saturated coal suggest that the angle of contact is about 90° but the value must in fact be less from the flotation experiments. It is concluded that a phase difference exists between water adsorbed on coal and bulk water.

British Coal Utilisation Research Association,
13, Grosvenor Gardens, London.

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[19] Bridgeman, *Physics of High Pressure* (London, 1931).
[20] Hardy, *Collected Scientific Papers* (Camb. Univ. Press, 1936).
[21] Batchelor and Foster, *Trans. Faraday Soc.*, 1944, **40**, 300.
[22] Rau, *Schrift. Deut. Akad. Luftfahrtforsch*, 1944, **8** (ii), 65; see also Frank, *Nature*, 1946, **157**, 267.
[23] Bangham, *Nature*, 1946, **157**, 733.
[24] Bangham, *J. Chem. Physics*, 1946, **14**, 352.

* According to Bridgeman,[19] liquid water cannot exist below *ca.* − 20° c., even under pressure; further, the pressures developed by the volume change on ice formation are too small to depress the freezing point sufficiently, even in an undeformable container.

PORE SIZE AND PORE DISTRIBUTION

By A. GRAHAM FOSTER

Received 17th February, 1948

In discussing the problem of estimating capillary radii of porous solids I shall deal here only with those methods based on experimentally determined sorption isothermals, which may be classified as follows.

(*a*) *Methods based on the Capillary Theory.*—The Kelvin equation when applicable gives the pore radius directly. The conditions under which the equation may be applied and the question of its validity will be discussed.

(*b*) *Methods based on Langmuir, B.E.T. or Harkins-Jura theories* in which the surface area of the solid is calculated from the sorption isothermals. I have shown [1] that an approximate estimate of the surface area can be made from the capillary radius using the relation $S/V = 2/r$ for the surface/volume ratio of a cylinder. Conversely, knowing S and V one can make a rough estimate of r, assuming that the pores are cylinders of uniform diameter. The chief application of the method would appear to be to systems where capillary condensation is absent and the Kelvin equation inapplicable.

(*c*) *Approximate estimates derived by considering the shape of sorption isothermals*, e.g., if sorption practically ceases after the formation of a monolayer, we may infer that the pore radius is of the order 1–2 molecular diameters. Following Brunauer,[2] I have discussed recently [3] how the shape of the isothermal alters as the number of adsorbed layers increases.

I. Application of the Kelvin Equation

(a) Radius-volume Curves.—In 1932, a modified version of Zsigmondy's capillary theory was proposed,[4] in which it was postulated (*a*) that condensation did not occur until after the formation of an adsorbed layer approximately two molecules thick, and (*b*) that over the range of the hysteresis area, desorption equilibria were determined by the Kelvin equation, assuming complete wetting, i.e.,

$$p_d = p_0 \exp(-2V\gamma/rRT) \quad . \quad . \quad . \quad (1)$$

where p_d is the desorption pressure, p_0 the saturation pressure, V the molar volume and γ the surface tension of the absorbed liquid at temperature T; r is the radius of curvature of the meniscus in the capillary over which the pressure p_d prevails and is usually identified with the radius of the capillary space in which condensation occurs.

According to the capillary theory, one would expect that (after converting pressures to radii and concentrations to volumes), pressure-concentration isothermals for *different* liquids would be reduced to the *same* radius-volume, or r-v, curve, the latter being determined by the structure of the adsorbent. This simple view ignores two factors: (*a*) the density of the adsorbed liquid may differ from that of the bulk liquid and thus lead to incorrect values of v; and (*b*) since condensation follows layer adsorption, the value of r calculated from the Kelvin equation is less than the true pore radius r_0 by an amount Δ equal to the thickness of the adsorbed layer.

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[1] Foster, *Proc. Roy. Soc. A*, 1934, **147**, 128.

[2] *Adsorption of Gases and Vapours* (Oxford, 1944). Ch. VI.

[3] Foster, *J. Chem. Soc.*, 1945, 769.

[4] Foster, *Trans. Faraday Soc.*, 1932, **28**, 645.

Although it was shown that isothermals for the *same* liquid at *different* temperatures reduced to identical *r-v* curves, yet it was not found possible to reduce isothermals of *different* liquids to the same *r-v* curve. The *r-v* curves for benzene and alcohol on ferric oxide were, however, identical in shape and could be made to coincide by displacement parallel to the axes. Lack of suitable experimental data has hitherto restricted further work on these lines, but an analysis has now been made of the isothermals of fifteen different liquids determined on ferric oxide by Broad and Foster.[5]

In the absence of detailed information about orientation of adsorbed molecules, we cannot determine accurately the thickness of the adsorbed layer but can only make an approximate estimate. This has been done by calculating molecular diameters (σ) from the normal density (d) of the liquid by means of the well-known relation

$$\sigma = 1{\cdot}33 \times 10^{-8}\left(\frac{M}{d}\right)^{1/3} \quad . \quad . \quad . \quad . \quad (2)$$

which assumes hexagonal close-packing and is similar to the relation used by Brunauer[2] for surface areas. If the Kelvin equation gives the radius r of the space left after completion of the adsorbed layer, assumed to be of thickness 2σ, then the true pore radius r_0 will be given by $r_0 = r + 2\sigma$, and for a given adsorbent, should be constant and independent of the nature of the adsorbed substance.

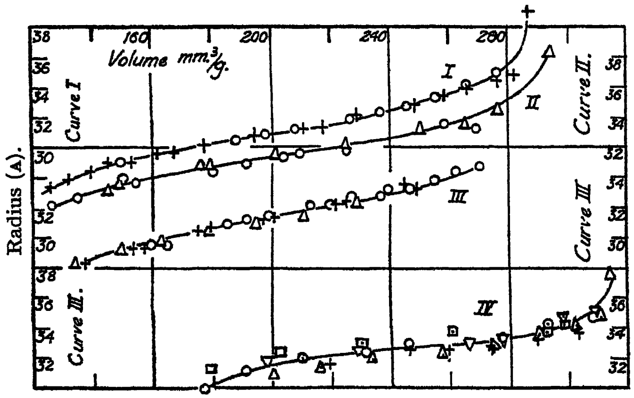

FIG. 1.

I. ○ EtOH + Dioxan.
II. ○ Morpholine Δ Triethylamine.
III. ○ *n*-hexane × $CHCl_3$ Δ Benzene.
IV. ○ EtOH Δ Dioxan + EtAc ▽ Butyl Acetate □ Pxylene.

Fig. 1 shows the data of Broad and Foster plotted as r_0 - v curves. Curve I is drawn through the points from the isothermals of ethyl alcohol and dioxan, which clearly coincide. The points on curve II are for triethylamine and morpholine, whilst the actual line represents curve I shifted to correspond with the displacement of the r scale. It is evident that within the limits of experimental error, the r_0 - v curves for all four liquids coincide. In curve III, data for *n*-hexane, benzene and chloroform are shown reduced to the same radius-volume curve, again with the r_0 scale shifted so as to avoid confusion with curves I and II. The latter can be brought very nearly into coincidence with curve III by vertical displacement corresponding to the shift of the r_0 scale. This means that isothermals for seven different liquids have been brought into virtual coincidence when plotted as $r_0 - v$ curves. Unfortunately, the data for the remaining substances investigated do not show such good agreement. Toluene and cyclohexane give a common curve, which lies 1·2 A. above curve I, whilst points for carbon tetrachloride lie about 0·5 A. above the latter; $r_0 - v$ curves for H_2O and D_2O coincide exactly but lie 2 A. below curve I, whilst *n*-octane lies 3 A. above. It was suggested by Broad and Foster that better agreement in this latter case would be obtained by assuming that the long-chain molecule lies flat in the adsorbed layer. Curve IV, which shows data for five different liquids reduced very nearly to the same radius-volume curve, is based on unpublished work by Batchelor and Foster on an " aged " sample of the ferric oxide gel used for the other experiments. It seems fair to conclude that if a more exact allowance for the thickness of the adsorbed layer could be made, radius-volume curves would, in general, coincide.

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[5] Broad and Foster, *J. Chem. Soc.*, 1945, 446.

(b) The Validity of the Kelvin Equation.—It is generally thought that this equation must break down when r approaches molecular dimensions, since both γ and V may then depart from their normal values, and a mathematical analysis of this question is urgently required. For the present, we can merely apply the equation in its usual form and seek independent confirmation of the correctness, or otherwise, of the calculated radii. It is obvious from the results just described that the equation remains valid for comparative purposes when the calculated radii are of the order 20 A., whilst the r-v curves of Broad and Foster[6] for H_2O and D_2O on silica gel, which coincide completely, show calculated values as low as 8 A. Crowther and Puri[7] measured the V.P. of water in soils and also made indirect measurements in which moist soil was shaken with benzene and the F.P. depression observed. Assuming that the V.P. in the latter systems was determined by the water-benzene interfacial tension in accordance with the Kelvin equation, good agreement between the two methods was found even when the calculated radii were below 10 A. Here again, we have no proof of the correctness of the calculated values but merely a demonstration of the apparent validity of the equation for comparative purposes.

The term $2/r$ which appears in eqn. (1) represents the surface/volume ratio of a cylinder and arises because when dn moles of liquid condense in a pore of radius r, the volume dv covers up free surface (of the adsorbed layer on the walls) $ds = 2\,dv/r$. Thus we should not interpret r too literally as a simple " radius." If the cross-section of the pores is not circular, the factor $2/r$ must be replaced by the corresponding value of ds/dv. We must also not attach too much importance to the approximate agreement between these r values and those calculated from the relation $r = 2$ (total volume adsorbed/g.) $\div$ (total surface area/g.) because this merely proves that $ds/dv = s/v$, and the numerical factor 2 may be incorrect in both cases. However, if the pores are uniform in shape we might expect, by comparing the values of r obtained by these two methods, to obtain some information on the manner in which the equation breaks down, since the second method involves no assumption about v or γ.

There are unfortunately few data available which give consistent values for surface areas in systems where capillary condensation also occurs. Emmett and de Witt[8] found hysteresis loops in the sorption of nitrogen, oxygen and argon on porous glass. Their radii calculated from $2s/v$, which they denote by r_V, average about 31 A. whilst the values derived from the Kelvin equation r_K average 22 A., so that addition of 8 A., representing two adsorbed layers, would give excellent agreement. Emmett and Cines [9] extended this work and quote figures for N_2,A and butane on several porous glasses which show good agreement between r_V and (r_K + 4) A. for one adsorbed layer, but the agreement would still be reasonably good for (r_K + 8) A., assuming two layers. The data of Broad and Foster do not give consistent values for the surface area of ferric oxide gel when values of σ^2, calculated from the density of the liquid, are used for the surface area per molecule. The figures for ethyl alcohol give $r_V = 37$ A. compared with $(r_K + 2\sigma) = 31$ A.

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[6] Broad and Foster, *J. Chem. Soc.*, 1945, 372.

[7] Crowther and Puri, *Proc. Roy. Soc. A*, 1924, **106**, 232.

[8] Emmett and de Witt, *J. Amer. Chem. Soc.*, 1943, **65**, 1253.

(c) Pore Distribution.—A point on a radius-volume curve represents the volume v required to fill all the pores having radii between 0 and r. The slope dv/dr indicates the volume dv required to fill those pores having radii between r and $r + dr$, hence a graph of dv/dr against r shows the extent to which pores of given radius contribute to the total volume. It has already been pointed out [4] that this curve corresponds roughly to a Gaussian distribution. Some typical volume-distribution curves are shown in Fig. 2; some are obviously not quite symmetrical, but none are very markedly skew, and all show a clearly defined maximum corresponding to the point of inflexion in the radius-volume curve and indicating the mean value of the capillary radius. In general, the smaller the mean radius the sharper the maximum, e.g., silica gel B with a radius of 10 A. shows a much sharper peak than ferric oxide B where the mean radius is 90 A. Higuti [10] observed a similar effect with a mixed gel of titania and ferric oxide. Raising the temperature of activation increased the pore radius and lowered the height of the distribution curve whilst at the same time the total volume was diminished. The ferric oxide gel investigated by Lambert and Foster showed the same behaviour after treatment with water.[4] It will be observed that some curves do not extend far to the left of the maximum. This is

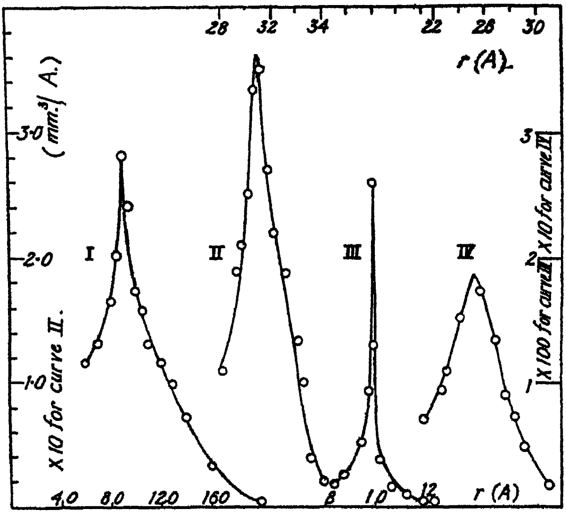

FIG. 2.

I Benzene-Fe_2O_3(B).
II. Dioxan + Alcohol-Fe_2O_3.
III. H_2O-SiO_2(B).
IV. H_2O-Al_2O_3.

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[9] Emmett and Cines, *J. Physic. Chem.*, 1947, 51, 1248.
[10] Higuti, *Bull. Inst. Phys. Chem. Res., Tokyo*, 1939, 18, 657

because condensation gives way to layer adsorption as the pressure falls, and we are then unable to apply the Kelvin equation. So far as capillary effects are concerned the axis should be shifted to correspond with the point at which hysteresis begins, and volumes reckoned from the start of the condensation process and not from the beginning of layer adsorption.

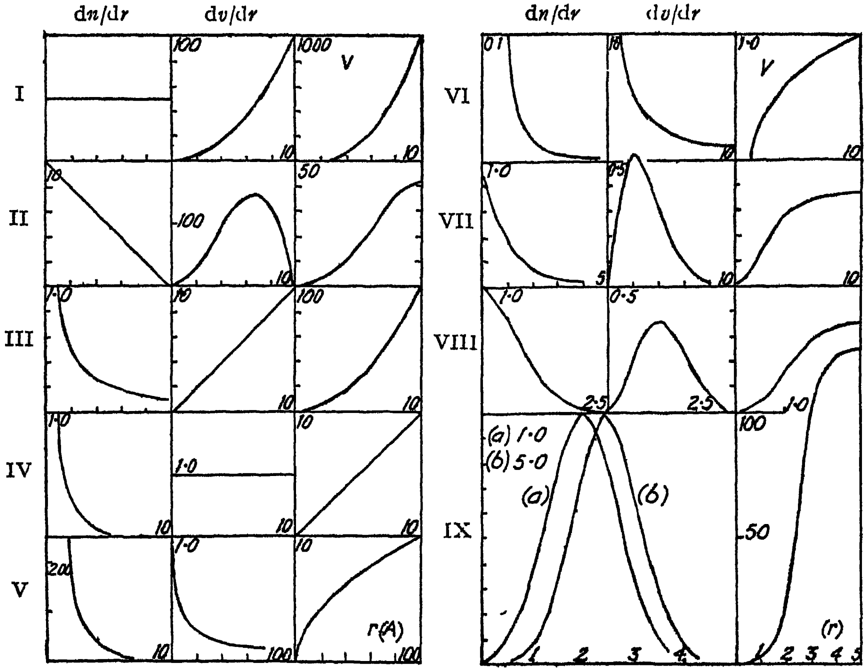


FIG 3.

KEY TO FIG. 3

	dn/dr	dv/dr	V
I	const.	ar^2	ar^3
II	$a - br$	$ar^2 - br^3$ (+*ve* values only)	$ar^3 - br^4$ (up to max)
III	a/r	ar	ar^2
IV	a/r^2	a	ar
V	$a/r^{5/2}$	$a/r^{3/2}$	$ar^{1/2}$
VI	a/r^3	a/r	$\log_e r$
VII	e^{-r}	r^2e^{-r}	$\int_0^\infty r^2e^{-r}dr$
VIII	e^{-r^2}	$r^2e^{-r^2}$	$\int_0^\infty r^2e^{-r^2}dr$
IX	$e^{-h^2(r-a)^2}$	$r^2e^{-h^2(r-a)^2}$	$\int_0^\infty r^2e^{-h^2(r-a)^2}dr$
	Curve (*a*) for $\left.\begin{array}{r}a = 2\\ h = 1\end{array}\right\}$	Curve (*b*)	

(Numerical constants omitted.)

The statement that the d*v*/d*r* curves show the pores to be distributed according to the normal law of probability is not strictly true. It is really the *number* of pores of different radii rather than their *volume* which we would expect to be distributed in this manner. The actual pores are most likely to be highly irregular spaces and cavities between coagulated particles of solid, the sizes of which are distributed around a mean. The Kelvin equation, as we have shown, interprets this complex structure in terms of a simpler structure of uniform non-intersecting cylinders of varying radii. If we assume these to have unit length, then the volume of any group of n cylinders of radius r is obviously $\pi r^2 n$. If then, there are $\mathrm{d}n$, such cylinders having radii between r and $r + \mathrm{d}r$, their volume will be $\mathrm{d}r = \pi r^2 \mathrm{d}n$. If we take the normal error function to denote the distribution of radii about the mean value a we shall have

$$\mathrm{d}n = k \exp\{-h^2(r-a)^2\}\mathrm{d}r \quad . \quad . \quad . \quad (3)$$

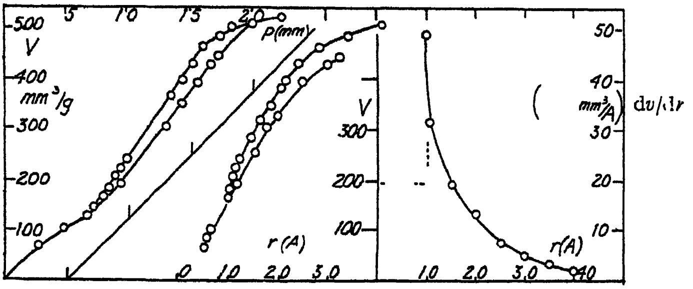
with a maximum at $r = a$

$$\therefore \quad \mathrm{d}v = \pi r^2 \mathrm{d}n = k\pi r^2 \exp\{-h^2(r-a)^2\}\mathrm{d}r \quad . \quad . \quad (4)$$

$\mathrm{d}^2v/\mathrm{d}r^2 = 0$ when $r^2h^2 - rh^2a - 1 = 0$ giving

$$r_{\mathrm{max}} = \tfrac{1}{2}\{a + (a^2 + 4/h^2)^{-\frac{1}{2}}\}$$

which reduces to $r_{\mathrm{max}} = a$ only when $h \gg a$. If the $\mathrm{d}v/\mathrm{d}r$ values for the curves in Fig. 2 are divided by r^2, no difference can be detected in the radii at which the maxima occur so we may infer that this condition is fulfilled for these systems.



H_2O—S_1O_2 System.

FIG. 4.

It is of interest to consider simpler distributions than that of eqn. (3). In Fig. 3 I have sketched roughly the curves of $\mathrm{d}n/\mathrm{d}r$, $\mathrm{d}v/\mathrm{d}r$ and v against r for a number of simple cases. It appears that the v-r curve will be concave to the v axis unless $\mathrm{d}n/\mathrm{d}r$ falls off at least as the $-5/2$ power of r (V). Case II is the simplest to give a curve resembling any actual v-r curve. A simple exponential decay $\mathrm{d}n/\mathrm{d}r = ae^{-r}$ also gives this type of curve (VII), which is also found even when one branch of the normal probability curve is missing, i.e., in the case $a = 0$, which makes $r = 0$ the most probable radius (VIII). The normal error function with $a = 2$ and $h = 1$ is shown in (IX*a*). The displacement of r_{max} from a is clearly shown in curve *b*.

It is difficult to say how far any of these distributions are likely to be realised in practice. All curves so far described show reasonable agreement with Case IX. A new sample of silica gel which has just been examined * gives the remarkable water isothermal shown in Fig. 4. The pressure is proportional to concentration between the limits 8–16 mm. (i.e., 150–450 mg./g.) covering practically the entire hysteresis area. The v-r curve has no inflexion over the range of capillary condensation and consequently the $\mathrm{d}v/\mathrm{d}r$ curve shows no maximum. I do not think this abnormal behaviour can be attributed to the disturbing effect of layer adsorption or to the smallness of the pore radii, since other silica gels show normal distributions down to 8 A. If the Kelvin equation is written in the form

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* Miss M. J. Brown (unpublished work).

$$x\ (= p/p_0) = \exp\ (-b/r),$$

and the linear range of the isothermal as $x = x_0 + av$, where v is reckoned from the beginning of capillary condensation, the curve will be represented by the relation,

$$\exp\ (-b/r) = x_0 + av$$

and

$$dv/dr = b/ar^2 \exp\ (-b/r),$$

or

$$dn/dr \propto e^{-b/r}/r^4,$$

a combination of exponential and inverse fourth-power decay. In theory dv/dr will have a maximum at $r = b/2$ which corresponds to $x = e^{-2} = 0{\cdot}135$, which is too low a relative pressure for condensation to occur ($r = 4$ A.).

Finally, since we have shown that the maxima of dv/dr and dn/dr do not in general coincide, we must consider whether we are justified in using the relation $s/v = 2/r$ for an assembly of non-uniform pores. For the surface and volume of a small number dn of pores between r and $r + dr$ we shall have

$$ds = 2\pi r dn \text{ and } dv = \pi r^2 dn$$

$$\text{whence } s = 2\pi k \int_0^\infty r \exp\ (-h^2(r-a)^2) dr$$

$$\text{and } v = \pi k \int_0^\infty r^2 \exp\ (-h^2(r-a)^2)\ dr$$

Evaluation of these integrals shows that there is no simple solution except when ah is large, when of course we get the expected result $s/v = 2/a$, where a is the " mean " radius

$$\frac{s}{v} = \frac{4h(2ah\sqrt{\pi} + 1)}{4a^2h^2\sqrt{\pi} + 4ah + \sqrt{\pi}} \simeq \frac{2ah^2\sqrt{\pi}}{a^2h^2\sqrt{\pi}}$$

Since we have already shown that the maxima of the dn and the dv curves coincide for the systems illustrated in Fig. 2, we may assume that the simple relation is also valid for these systems. Obviously, however, we must use this relation with care especially when the distribution curve is flat or unknown.

II. Determination of Surface Areas

Comprehensive reviews have been given by Brunauer[11] and Emmett.[12] Methods based on actual sorption measurements from the gas phase fall into two classes (i) based on the Langmuir equation and hence on measurements carried out whilst the monolayer is actually being formed, and (ii) based on the multilayer theory, where the amount v_m required to complete the monolayer is obtained by extrapolation from the region of multi-layer adsorption. In endeavouring to calculate the surface area by these methods the common difficulty is to choose a suitable value for the area occupied by a single adsorbed molecule. In the absence of definite information about molecular orientation it is customary to use the value of σ^2 calculated by eqn. (2).

(a) Langmuir Method.—The linear plot

$$p/q = 1/zb + p/z \quad . \quad . \quad . \quad . \quad (5)$$

enables the saturation value z to be determined easily. A number of low-pressure isotherms which obey this relation have been described recently[13] and I have indicated how a correction for multilayer adsorption can be applied in favourable cases.[14]

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[11] Ref.[3] Ch. IX.

[12] *Advances in Colloid Science* (New York, 1942), Vol I.

[13] Foster, *J. Chem. Soc.*, 1945, 360.

(b) B.E.T. Method.—The fundamental equation of the B.E.T. theory is

$$\frac{p}{v(p_0 - p)} = \frac{1}{v_m c} + \frac{(c-1)p}{c v_m p_0} \quad . \quad . \quad . \quad . \quad (6)$$

where v is the actual amount adsorbed at pressure p, and v_m the amount required to complete the monolayer. The equation is derived by summation over an infinite number of layers and, in practice, a linear relation is not found over a very wide range. I have discussed elsewhere some of the simple limiting cases which might reasonably be expected.[15] Examination of the now extensive adsorption data for non-porous solids fails to reveal any systems which show particularly good agreement with the limiting case $v/v_m = p_0/(p_0 \text{-} p)$ which arises when the heat of sorption in the first layer is large and c large.

(c) "Point A" and "Point B" Methods.—These were derived before the development of the multilayer theory and apply only to isothermals with a linear middle portion which begins at "point B" and extrapolates to zero pressure at "point A." I have already shown[14] that when low-pressure data are available the "point A" values agree well with those obtained from the Langmuir equation, and also that there is some theoretical basis for the "point A," but not for the "point B" method.

(d) Harkins-Jura "Absolute" Method.—If a non-porous solid covered with an adsorbed film in the presence of saturated vapour is immersed in bulk liquid heat H is evolved given by $\Sigma = 4{\cdot}185 \times 10^7 H/h$, where Σ is the surface area and h the total surface energy $\gamma - T\mathrm{d}\gamma/\mathrm{d}T$. Σ may thus be determined calorimetrically without assumptions about surface areas of molecules. The area of a sample of anatase (TiO_2) found by this method[16] agreed closely with the value found by the B.E.T. method taking $\sigma^2 = 16{\cdot}2$ A.^{2} for N_2. The method is also applicable to porous solids since the heat change accompanying capillary condensation is a similar effect. The data of Lambert and Clark[17] for benzene or ferric oxide show an integral heat of sorption over the hysteresis area of 2·30 cal., which with $h = 66$ erg./cm.^{2} gives $\Sigma = 1{\cdot}44 \times 10^6$ cm./g. Direct application of the Kelvin equation gives $r = 16$ A., whence $\Sigma = 2v/r$, where v is the volume range of the hysteresis loop = 0·115 cm.^{3}, giving $\Sigma = 1{\cdot}44 \times 10^6$. This is, of course, the surface of the adsorbed layer which is less than the true surface of the solid in the ratio $r/(r + \Delta)$, where Δ is the thickness of the layer.

(e) Harkins-Jura "Relative" Method.—According to these workers,[18] condensed films in monolayers follow the empirical relation

$$\pi = b - a\sigma_m \quad . \quad . \quad . \quad . \quad (7)$$

where π is the surface pressure (formerly denoted by F) and σ_m (formerly A) the area available per molecule in the surface layer, defined by

$$\sigma_m = M\Sigma/Nq \quad . \quad . \quad . \quad . \quad (8)$$

where M/q is the adsorption in mole/g. and Σ the specific surface. Eqn. (7) may be substituted into the Gibbs' equation

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[14] Foster, *J. Chem. Soc.*, 1945, 773.

[15] Foster, *J. Chem Soc.*, 1945, 769.

[16] Harkins and Jura, *J. Amer. Chem. Soc.*, 1944, **66**, 1362.

[17] Lambert and Clark, *Proc. Roy. Soc. A*, 1929, **122**, 497.

[18] Harkins and Jura, *J. Amer. Chem. Soc.*, 1946, **68**, 1941.

$$d\pi = (\boldsymbol{RT}/M\Sigma)q \, . \, d \log_e p \qquad (9)$$

giving

$$d \log_e p = \{a(M\Sigma)^2/\boldsymbol{NRT}\} dq/q^3 \qquad (10)$$

which on integration gives the Harkins-Jura isotherm,

$$\log_e p = B - A/q^2 \qquad (11)$$

where $A = a(M\Sigma)^2/2\boldsymbol{NRT}$,

or $\Sigma = kA^{\frac{1}{2}}$, where $k^2 = 2NRT/aM^2$, and is assumed to be characteristic of a given adsorbate at a given temperature, independent of the nature of the adsorbent; k can be evaluated from a single experiment by the absolute method on a non-porous solid and this value used for other adsorbents, porous or non-porous, at the same temperature.[19]

TABLE I

Molecule	Area per Molecule (A.^{2})				
	1	2	3	4	5
H_2O	10·8	14·8	10·6	—	19·5
A	13·7	—	—	-	15·4
NH_3	13·8	—	—	-	15·4
CO_2	14·2	—	-	-	20·1
C_2H_2	15·2	—	—		22·2
Kr	15·2	—	-	20·8	—
N_2	16·2	16·1	15·4	16·2	16·2
$CHCl_2F$	26·4	—	—	40·0	—
I-Butene	30·5	—	—	42·7	—
n-C_3H_7OH	31·3	—	20·0	—	—
n-C_4H_{10}	32·0	56·6	—	47·0	49·0
n-C_7H_{16}	45·0	64·0	55·0	—	—

Column 1.—Calculation from eqn. (2).
„ 2.—Harkins and Jura.[19] Calculation for best fit of B.E.T. Method with H.J. method. (TiO_2, $ZrSiO_4$, $BaSO_4$, SiO_2.)
„ 3.—Livingston.[22] (SiO_2, TiO_2, $BaSO_4$. Graphite.)
„ 4.—Davis, de Witt and Emmett.[23] (Metal foil, glass spheres. Al_2O_3, SiO_2, ZnO, W.)
„ 5.—Emmett and Cines.[9] (Porous glass.)

Livingston [20] and Emmett [21] have both considered the compatibility of the B.E.T. theory with the Harkins-Jura relation and conclude that, if a given set of data follow the B.E.T. equation, the H.J. method will not give a linear plot unless the B.E.T. constant c is at least 50. The value of σ^2 needed to make the two methods agree increases with c, e.g., from 13·6 to 24·6 A.^{2} for N_2 as c changes from 50 to 1000. On the one hand, Harkins and Jura [18] criticise the B.E.T. assumption of constant molecular area for a given adsorbate and on the other, Emmett [21] criticises the assumption that k, which depends on a in eqn. (7), is independent of the adsorbent. In spite of the apparent agreement between the two methods obtained by Harkins and Jura,[19] we must remember that both theories are empirical, the H.J. theory because it uses an empirical relation (7) to integrate the Gibbs' equation and the B.E.T. because its fundamental assumption is untrue, viz., that the net heat of sorption is zero for all layers after the first. Harkins and Jura [18] having determined Σ by the absolute method used the B.E.T.

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[19] Harkins and Jura, *J. Amer. Chem. Soc.*, 1944, **66**, 1366.
[20] Livingston, *J. Chem. Physics*, 1947.
[21] Emmett, *J. Amer Chem. Soc.*, 1946, **68**, 1784.
[22] Livingston, *J. Amer. Chem. Soc.*, 1944, **66**, 569.
[23] Davis, de Witt and Emmett, *J. Physic. Chem.*, 1947, **51**, 1232.

method to determine the monolayer adsorption and then calculated σ^2 per molecule of N_2. For 86 different solids, they quote 16 different values, grouped mainly round three peaks at 14·05, 15·25 and 16·05 A.^{2}. The smallest area 13·6 lies close to that calculated from the density of solid N_2 and the largest 16·8 lies close to that calculated from the density of liquid N_2.

In Table I, I have collected the available data for "observed" surface areas per molecule. The fact that the product $(z/M)\ \sigma^2$ is not constant when the values of column 1 (calculated from eqn. (2)) are used is surprising since both Goldmann and Polanyi[24] on charcoals and Broad and Foster[25] on silica gel B found excellent agreement. On silica gel A, the latter workers found that the product decreased with increasing molecular diameter, and that z/M gave a linear plot against $1/\sigma^2$ which no longer passed through the origin. This was attributed to the presence of tapering capillaries about 10 A. wide at their open ends. None of the results quoted in Table I appears to be capable of interpretation in a similar manner and we are thus left in a most unsatisfactory position. The problem is probably related to that arising in the discussion of volume-radius curves, i.e., if the area of the monolayer cannot be estimated from the "normal" cross-sectional area σ^2, we cannot expect σ itself to represent accurately the "thickness" of the adsorbed layer, since both are calculated from eqn. (2). At present, I can only suggest some such explanation as that proposed by Herington and Rideal,[26] who pointed out that if a hexagonal molecule had to be attached to fixed points in the lattice of the solid at all its corners, the surface would never be completely covered and even at saturation as much as 35 % might be bare. It is difficult, however, to see how such an explanation could apply to small and simple molecules like N_2 and A.

III. The Shape of Sorption Isothermals

When condensation occurs and can be recognised as such, e.g., by the appearance of a hysteresis loop, we can apply the Kelvin equation to determine the pore radius. The smallest calculated radii at which condensation appears are of the order 10 A. Thus, water on silica gel shows hysteresis from 11 A. down to about 8 A. whilst other liquids show mean radii of about 15 A. on silica and titania gels. Taking 5 A. as an average molecular diameter, a calculated radius of 15 A. corresponds to a true pore radius about five times the molecular diameter, if the adsorbed layer is two molecules thick. It follows that our remaining problem—how to estimate pore size when condensation does not occur—is concerned with the behaviour of systems in which $r/\sigma < 5$. We can recognise the cases where $r/\sigma = 1$ or 2 by the fact that unimolecular adsorption then accounts for virtually the entire sorption process, and are thus left with r/σ varying from 3–5 as the cases to be identified.

I have already shown[15] that when n is put equal to 2 or 3 the B.E.T. theory predicts linear isothermals. The effect of the curvature of the surface of the adsorbent, which is ignored by this theory, has been considered by Broad and Foster[5] who showed that isothermals for $n = 4 - 6$ at curved surfaces would assume roughly the same shape as those for which $n = 2 - 3$ at a plane surface. We can thus regard the linear isothermals found for alcohols on silica gel as representing the intermediate case where n lies between $2 - 6$. (The converse argument that $n = 2 - 6$ necessarily gives a linear isothermal does not apply since the magnitude of the heat of sorption is also involved.)

[24] Goldmann and Polanyi, *Z. physik. Chem.*, 1928, **132**, 356.
[25] Broad and Foster, *J. Chem. Soc.*, 1945, 366.
[26] Herington and Rideal, *Trans. Faraday Soc.*, 1944, **40**, 505.

A further check can be made by using the relation $r = 2v/s$, but a simpler method is to calculate the ratio of the monolayer to the total sorption (z/q_s). The percentage of total volume of a cylinder represented by the first layer has the following values :

n	1	2	3	4	5	6	7	8	9	10
z/q_s (%)	100	75	55	44	36	30	26	23	21	19

Thus, when we find $z/q_s = 51$ for ethyl alcohol on silica gel B, we suspect n to lie between 3 and 4 which would give $r = 15 - 20$ A. On the same gel, water shows a large hysteresis loop with mean radius 10 A. corresponding to a true radius of 16 — 17 A. if two layers are present.

Summary

The determination of capillary radii of porous solids by application of the Kelvin equation, from estimates of surface area and indirect methods, is discussed. It is shown that radius-volume curves for different substances on a given adsorbent can be made to coincide when allowance is made for the thickness of the adsorbed layer. Volume-distribution curves, showing how far pores of given radius contribute to the total pore-volume, are described for SiO_2, Fe_2O_3 and Al_2O_3 gels, and the effect of different distribution of pore radii on the shape of the isothermal is discussed. It is suggested that the difficulty of estimating molecular surface areas encountered in applying the B.E.T. and other adsorption methods to the determination of surface areas is related to the difficulty in estimating the thickness of the adsorbed layer which is encountered in applying the capillary theory.

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MEASUREMENT OF INTERNAL SURFACE BY NEGATIVE ADSORPTION

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The purpose of this paper is to show how measurements of the small increase in concentration that occurs when a salt solution is shaken up with a sample of dry fibre may be used, in certain circumstances, to calculate both the internal surface and the volume of pore space inside the fibres. The theoretical background is provided by Gouy's[1] theory of the ionic distribution in the diffuse component of the electric double-layer, which the first-named author[2] has extended to obtain an expression for the negative adsorption of the ions electrostatically repelled from the phase boundary. With mathematical help from Dr. M. H. Quenouille he obtained, for the case when all the attracted ions have valency v and all the repelled ions have valency v/p, the expression

$$\frac{\Gamma_-}{n} = \frac{q}{\sqrt{v\beta n}} - \frac{4}{v\beta\Gamma} \quad . \quad . \quad . \quad . \quad (1)$$

as a good approximation, provided the first term is several times the second.

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[1] *J. Physique*, 1910, **9**, 457.
[2] *Nature*, 1947, **160**, 408.

Here n is the electrolyte concentration in m.equ./cc., and Γ is the total charge in the diffuse layer expressed in m.equ./cm.^{2}. Γ_- is the part of Γ due to the deficit of repelled ions. β stands for $8\pi F^2/\varepsilon RT$, so that $\nu\beta$ has the value $1{\cdot}06\nu \,.\, 10^{15}$ cm./m.equ. for water at 20° C. q depends on the valency ratio, p, in the manner shown in Table I, where the entries to four decimal places have been directly calculated, and the rest obtained from them by a graphical method.

TABLE I

Valency Ratio p	Factor q
0	3·1416 (π)
1/7	2·91
1/6	2·88
1/5	2·83
1/4	2·76
1/3	2·65
1/2	2·4495 ($\sqrt{6}$)
1	2·0000
3/2	1·69
2	1·4641 ($\sqrt{12}-2$)
3	1·16
4	0·96

Eqn. (1) has been worked out for the case of a plane interface and an infinite depth of liquid in which the ions are in ideal solution, and caution must be exercised in applying it to a natural fibre in a real salt solution. Still assuming ideal solution, an examination of the case, where two parallel and opposed interfaces are separated by a finite distance $2X$, shows that when $\nu\beta\Gamma X$ is less than about 10,

$$\frac{\Gamma}{nX} = \left(1 - \frac{\Gamma_-}{nX}\right)^{-p} - \left(1 - \frac{\Gamma_-}{nX}\right) \quad . \quad . \quad . \quad (2)$$

approximately. Eqn. (2) is, in effect, Donnan's equation for the membrane equilibrium in the form $(z/x) = (y/x)^{-p} - (y/x)$. Hence, if $\nu\beta\Gamma X$ is too small, (1) is not valid at any value of n. If, however, $\nu\beta\Gamma X$ exceeds about 30, eqn. (1) can be applied for values of $q/\sqrt{\nu\beta n}$ between about $15/(\nu\beta\Gamma)$ and $X/2$ (values computed for $p = 1$). The approximation is closer the wider this gap.

Whatever the value of $\nu\beta\Gamma X$, the equation

$$\frac{\Gamma_-}{n} = X - bn^{1/p} \quad . \quad . \quad . \quad . \quad (3)$$

holds approximately when $bn^{1/p}$ is a small fraction of X, b being a constant depending on p, $\nu\beta$, Γ and X. The extrapolation, used below to obtain the volume of the pore space, is based on this approximation.

The main effect of departures from ideal solution as in eqn. (3) of specific adsorption of the attracted ions and of hydration effects close to the interface is to increase or decrease the part of Γ_-/n that is independent of n. Thus the slope of the graph of Γ_-/n against $1/\sqrt{n}$ should be close to $q/\sqrt{\nu\beta}$ within the range of n appropriate to eqn. (1), but these disturbances will prevent us from obtaining Γ from the intercept.

No precise treatment of the effects of curvature of the interface has been attempted. It is clearly desirable that the principal curvatures should everywhere be small compared with $\sqrt{\nu\beta n}$. Even when this is not true in detail, some compensation may arise between portions of the interface having opposite curvatures. The area obtained below for the internal surface of jute fibres must be regarded as the equivalent area of a plane interface.

Experimental

One sample of retted " white " jute and two of retted " red " jute, kindly given by the Indian Jute Mills Association, which we will distinguish by the letters A, B and C, were milled, and then steeped in N./100 Na_2CO_3 solution in order to hydrolyse ester linkages. They were then washed with water until small test samples, when shaken up with N. KCl solution, showed a pH value a little below 7.* The samples were then divided into parts which were washed with Li, Na, K and Ca chlorides respectively, and then with water, until they were free of chloride. These sub-samples were air-dried at room temperature, and stored in desiccators over $CaCl_2$. The *p*H values determined in N. KCl were all close to 6.

10 g. portions of the calcium-treated jutes were leached with KCl solutions, and the exchangeable calcium released was determined. In this way the number, *E*, of milliequivalents of negatively charged groups (mainly $-COO^-$ groups) attached to 100 g. of dry fibre was found for each sample, the loss of water on drying at 105° C. having been determined on separate portions.

Experiments were made on sample C using Li, Na, K and Ca chlorides at concentrations from N./128 to N. The strongest solutions were not used in experiments with samples A and B, since it is doubtful whether a theory that postulates ideal solution can usefully be applied to solutions more concentrated than N./10. The experiments on sample A were made with Na and Ca chlorides, and on sample B with KCl also.

In each experiment, a 10 g. portion of the sub-sample containing the appropriate cation was weighed into a dry flask. After adding 200 cc. of the test solution, the flask was tightly stoppered, shaken several times, left standing overnight and again shaken well next morning. A convenient volume of the resulting solution was then delivered into a second dry flask, and weighed, and its chloride content was determined by the Volhard method. A parallel determination was also made of the chloride in a similar weighed volume of the original solution. The small increase, Δn, in the concentration could usually be estimated to about 3 %, the determinations for the strongest solutions being least exact. For each experiment the percentage moisture, *m*, in the fibre (dry basis) was determined by drying a separate 5 g. portion in an oven at 105° C.

In order to find out how much of the observed effect must be ascribed to agencies other than the negative charges, parallel experiments were made with solutions containing N./20 HCl. As these solutions have *p*H 1·3, most of the carboxyl groups were in the uncharged $-COO^-$ condition. The weakest of these solutions contained only N./20 HCl except for the small number of metallic ions released from the fibre. The next contained the salt in addition at N./20, making the total chloride concentration N./10. Only with sample C were these experiments taken up to normal chloride. A base-free sub-sample was prepared from sample C by washing it first with HCl and then with water until it was free of chloride. This, when dry, produced concentration changes in N./20 HCl that increased with the time of storage, indicating an instability of structure.

Results

It is convenient to distinguish by the suffixes 6 and 1·3 the results obtained at *p*H 6 and *p*H 1·3 respectively, and to define v_6 by the equation

$$v_6 = 20(100 + m)\frac{\Delta n_6}{n} + m \quad . \quad . \quad . \quad . \quad (4)$$

with a similar equation for $v_{1\cdot3}$. A set of values for sample C in NaCl solutions is set out in Table II.

It will be seen that $v_{1\cdot3}$ rises with fall in *n* to a maximum value which is practically attained at N./10. Although it is impossible to obtain *p*H 1·3 in solutions weaker than N./20 it is reasonable to consider that 11 cc. per 100 g. is the part of v_6 not due to the negative charges at all concentrations below N./20. This 11 cc. presumably represents water inside the fibre substance from which chloride ions are completely excluded owing to their size. It corresponds to the 12·5 cc. of water which has been observed by Sookne and Harris[3] to be taken from acid solutions by cotton.

The cause of the fall in $v_{1\cdot3}$ with rise in *n* above N./10 cannot be given with certainty. It may indicate a positive adsorption of chloride occurring when the electrical potential in the solution in contact with the internal surface of the

[3] *Text. Res.*, 1940, **10**, 405.

* For the basis of this technique, see Saric and Schofield, *Proc. Roy. Soc. A*, 1946, **185**, 431.

fibre is only slightly less than that in the bulk of the solution. This effect would diminish rapidly with reduction in salt concentration because the concentration of chloride ions against the surface is further reduced by the mounting difference in electrical potential.

TABLE II—NEGATIVE ADSORPTION OF CHLORIDE BY JUTE
(Sample C in NaCl)

Chloride conc n	v_6 (pH 6) cc /100 g	$v_{1\cdot 3}$ (pH 1·3) cc /100 g.	Difference v_E cc /100 g	$\frac{q}{\sqrt{\nu\beta n}}$ A
1·0	15·1	7·3	7·8	6·1
0·5	23·7	8·8	14·9	8·6
0·2	32·7	10·2	22·5	13·7
0·1	40·3	10·9	29·1	19·3
0·05	34·2	11·0	43·2	27·3
0·025	59·4	(11·0)	48·4	38·6
0·0125	72·2	(11·0)	61·2	54·6
0·00625	79·4	(11·0)	68·4	77 2
0 0	(86·0)	(11·0)	(75·0)	∞

The quantity of greatest interest is the difference v_E between v_6 and $v_{1\cdot 3}$, for this is the direct consequence of the presence at pH 6 of E m equ. of negative charges per 100 g. A plot of v_E against n (cp.eqn. (3)) shows that v_E is tending to the limit, V, when n is very small. V for sample C is 75 cc. per 100 g. This is evidently the volume of the water-filled pore space which is freely accessible to chloride ions when the internal surface is uncharged, but from which chloride ions tend to be excluded when it is negatively charged.

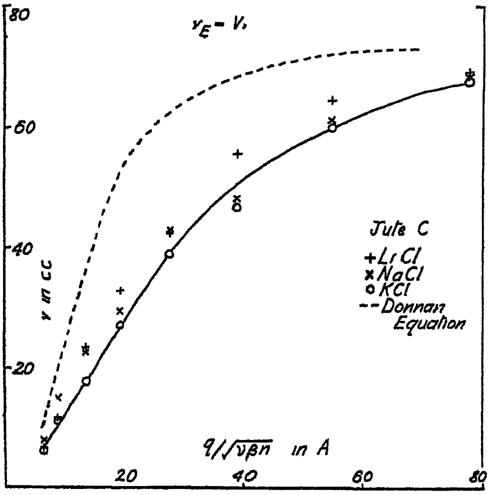

FIG. 1

In order to show how eqn. (1) can be used to obtain the internal surface the experimental values of v_E for sample C in Li, Na, and K chlorides are plotted in Fig. 1 against $q/\sqrt{\nu\beta n}$. There is a distinct tendency for the points for LiCl to be above, and those for KCl to be below, the points for NaCl; but there is no indication of any difference in slope at the higher concentrations or in V. Only one curve has therefore been drawn. The equivalent plane area, A, obtained from the slope of the straight portion is $1{\cdot}5 \times 10^8$ cm.^{2} per 100 g., or 150 m.^{2} per g. Dividing E by A we get $1{\cdot}47 \times 10^{-7}$ m.equ./cm.^{2} for Γ, so that $15/\nu\beta\Gamma = 11$ A. Dividing V by A we get 50 A. for X so that $X/2 = 25$ A. Hence we were justified in using the slope between these limits to obtain A. As a further check, values for v_E were calculated by means of Donnan's equation, and these were used to construct the broken curve. This falls well above the experimental points where they have been used to obtain the internal area. Thus the conditions that must be fulfilled when (1) is used to obtain the equivalent plane area are satisfied in the case of sample C. The value thus obtained for A is roughly a thousand times the external surface of the fibres.

The results for sample B (the other sample of "red" jute) are similar to those for sample C, but those for sample A (the "white" jute) plotted in Fig. 2 are strikingly different. When the Donnan curve was constructed it was found to fit the experimental points for NaCl within the limits of experimental error. Eqn. (1) cannot, therefore, be used to obtain the internal surface of this sample.

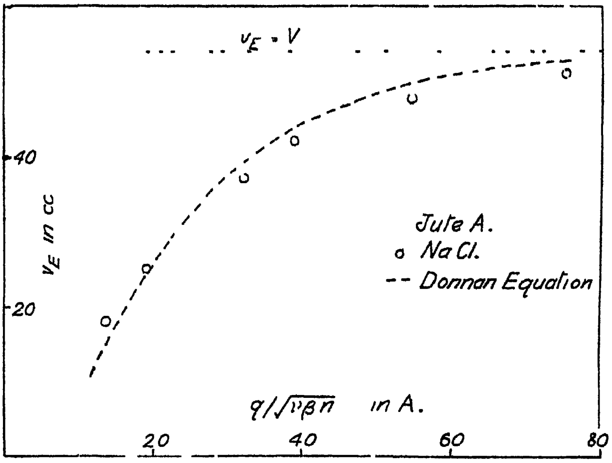

FIG. 2

The information obtained about the internal pore space of the three samples of jute from experiments with solutions of the alkali chlorides is summarised in Table III. The values in parenthesis are based on considerations given in the discussion.

TABLE III

	White Jute Sample A	Red Jute Sample B	Red Jute Sample C
E m.equ./100 g.	6·6	16·0	22·0
V cc./100 g.	54	68	75
A m.^{2}/g.	(200)	130	150
Γ m.equ./cm.^{2}	(0·33 . 10^{-7})	1·23 . 10^{-7}	1·47 . 10^{-7}
X A.	(27)	52	50

The results obtained with $CaCl_2$ were not entirely concordant. For this salt $q/\sqrt{\nu}$ is 1·03 compared with 2 for the alkali chlorides, and the results obtained with samples B and C generally reflect this difference. Three experiments with sample A gave points that all lie below the Donnan curve. If these results can be confirmed and extended, they may enable us to make a rough estimate of the surface area.

Discussion

The value of Γ obtained for sample C, if interpreted as a uniform surface distribution of negatively charged groups, gives an average distance of about 12 A. between neighbouring groups, while the value of X indicates that, on an average, the surfaces are separated by about 100 A. It is, therefore, quite reasonable to picture these groups as giving rise to an ionic distribution of the Gouy type.

On general grounds it is likely that, in sample A also, the negative groups are distributed over an internal surface. The close fit of the points in Fig. 2 to the Donnan curve indicates that $\nu\beta\Gamma X = \nu\beta EV/A^2$ cannot much exceed 10, so A cannot be much less than 200 m.^{2}/g. This value gives 0·33 × 10^{-7} m.equ./cm.^{2} for Γ and 27 A. for X. In this case, the negative groups would be spaced at about 25 A. on the internal surfaces which would on an average be separated by about 50 A. In this case it is not to be expected that the Gouy treatment would be applicable. Since it appears that the negative groups are distributed nearly uniformly through the *volume* of the pore space, we would expect Donnan's equation to hold as Procter [4] found it to do in the case of swollen gelatine. On the other hand, the Congo Red studied by Donnan and Harris [5] did not obey Donnan's equation very closely, presumably because the $-SO_3^-$ groups are not uniformly dispersed in the solution but clustered on the surfaces of micelles.

Summary

An extension of Gouy's treatment gives the equation

$$\frac{\Gamma_-}{n} = \frac{q}{\sqrt{\nu\beta n}} - \frac{4}{\nu\beta\Gamma} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

for the negative adsorption Γ_- of the repelled ions in the diffuse part of the electric double-layer. The conditions under which this equation can be applied and the errors that may arise in non-ideal conditions are set out.

Measurements have been made at *p*H 6 and *p*H 1·3 of the small increase in concentration occurring when samples of jute are shaken up in chloride solutions, the concentration, n, ranging from N. to N./128. At *p*H 1·3, the volume $v_{1\cdot 3}$ of water taken by 100 g. of dry jute is close to 11 cc. for concentrations below N./10. This water is presumably taken into the fibre substance where chloride ions cannot enter. At *p*H 6 the volume v_6 is greater than $v_{1\cdot 3}$. The difference, v_E, must be due to the influence of the negatively charged groups. Their amount, E, was determined for each of the three samples of jute by cation exchange. The limit, V, of v_E as $n \to 0$ is the volume of the pore space which ranges from 50 to 75 cc. per 100 g.

In the case of two samples of " red " jute all the conditions for the application of eqn. (1) were fulfilled over a sufficient range of concentration for the equivalent plane area, A, of the internal surface to be obtained from the slope of the graph of v_E against $q/\sqrt{\nu\beta n}$. It is roughly a thousand times the external surface of the fibres. In the case of a sample of " white " jute the conditions are not fulfilled, and the results follow Donnan's equation for the membrane equilibrium. In the " red " jute the average separation of negative (mainly $-COO^-$) groups on the internal surface is about 12 A. and the average width of the pore space about 100 A. In the " white " jute the groups are at least 25 A. apart on the surface and the average width of the pore space does not exceed 50 A.

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[4] *J. Chem. Soc.*, 1914, **105**, 313.
[5] *J. Chem. Soc.*, 1911, **99**, 1554.

IONIC DIFFUSION AND ELECTRICAL CONDUCTIVITY IN SANDS AND CLAYS

By R. K. Schofield and C. Dakshinamurti

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It has often been suggested, but never proved, that water in fine pores suffers a modification of its properties through the operation of long-range forces. It appeared possible that a quantitative study of the migration of ions through media having pores of widely different sizes might provide new evidence. In any case, since ions diffuse through soil to plant roots, a study of ionic diffusion in porous media more or less resembling soil appeared very desirable.

As none of the methods hitherto used appeared suitable, a new technique has been developed. In order to simplify the underlying theory, all our diffusion experiments have been carried out under conditions of constant total ionic concentration. Thus, when N./10 KBr and N./10 KNO_3 come into contact there is an inter-diffusion in which the sum of the nitrate and bromide concentrations remains practically unaltered. This is because the nitrate ion has nearly the same mobility as the bromide ion. Were their mobilities exactly equal, the diffusion process would be governed by a single diffusion constant for any given total concentration and temperature. In the more general case represented by the inter-diffusion of N./10 KBr and N./10 NH_4NO_3, there are two diffusion constants, one for the anions and another for the cations.

Theoretical

Imagine that two still solutions, A and B, containing ions of equal mobilities, but chemically distinguishable, and of the same concentration, C_O, are brought into contact at a plane surface. The ions of solution A will at once start to diffuse into solution B, and vice versa. From considerations of symmetry it is evident that, in the plane where contact was made, the ionic concentrations will immediately fall to, and remain at, $C_B = \frac{1}{2}C_O$. Following the treatment of Einstein[1] the amount, q, of ions that diffuse across area A of this plane in time τ is related to the diffusion coefficient, D, and the root mean square displacement of an individual ion, $\bar{\Delta x}$ by the equation,

$$\sqrt{\frac{\pi}{2}} \cdot \frac{q}{C_B A} = \sqrt{2D\tau} = \bar{\Delta x} \quad . \quad . \quad . \quad . \quad (1)$$

For diffusion into a solution of depth $1{\cdot}5\ \bar{\Delta x}$, q is only $0{\cdot}2$ % less than for diffusion into a solution of infinite depth.

If one of the two solutions was held in a system of parallel channels occupying only a fraction, f, of the total cross-section, ions initially at concentration C_O in these channels would maintain a concentration C_B at the boundary such that

$$C_B = \frac{f}{1+f} \cdot C_O \quad . \quad . \quad . \quad . \quad (2)$$

In this case if q, A, f and C_O are measured, D is obtained by combining eqn. (1) and (2).

If one of the solutions is held in a porous bed, C_B can be determined by (1), if q, A and τ are measured and D is known. An effective value of f can then be obtained by using (2).

Experimental

Tubes of about 0·5 mm. bore and external diam. 2·0 mm. were cut to a length of 4·5 cm. and ground at both ends. They were tightly packed in the lower part of a flat-bottomed cylindrical vessel so that the ground ends were level. The space inside and between the tubes was filled with N./10 KBr solution, and the excess KBr solution on top of the ground surface was removed. The volume of the liquid that filled the capillaries was obtained by weighing, and the fractional area, f, was calculated. In the first two experiments N./10 KNO_3 solution, and in the subsequent experiments N./10 NH_4NO_3 solution, was placed above the tubes to a height of 4·5 cm. The solution was delivered slowly through a capillary tube, bent up at the end, which was held against the wall of the vessel and raised as the filling proceeded so as to cause as little mixing as possible. Even if there is slight mixing, its effect on the total amount of the ionic diffusion will be insignificant since it amounts to shifting the time of starting the experiment by a few minutes only, the amount diffused being proportional to the square root of the time of diffusion. During the diffusion, the upper end of the vessel was closed with a ground-glass plate smeared with grease to prevent evaporation. The experiments were conducted in a constant temperature room at about 20·5° c.

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[1] Einstein, *Ann. Physik*, 1905, **17**, 549.

The choice of the electrolytes used in the experiments was based on two considerations. (1) The density of the KBr solution which filled the lower part of the vessel is greater than that of either the KNO_3 or NH_4NO_3 solution of the same concentration. This ensures that the mixing is not due to the density differences. (2) It is known from conductivity data that the mobility of the NO_3^- ion is only a little less than that of the Br^- ion, and the agreement between the mobilities of the K^+ and NH_4^+ ions is even closer. The amount of bromide found in the upper solution will thus give very nearly the diffusion coefficient of the Br^- ion in N./10 KBr or N./10 NH_4Br solutions. At the same time, the ammonium found in the lower solution should give even more closely the coefficient for the NH_4^+ ion in N./10 NH_4NO_3 or N./10 NH_4Br.

After a measured time the upper liquid was removed with a pipette fitted with a hypodermic needle. The amount of solution left in the lower part was checked by re-weighing, and the appropriate correction was applied in calculating the amount diffused. This correction, however, was usually less than 1 %. The solution that was removed would contain the K^+ and Br^- ions that diffused upwards and would be depleted by the K^+ and NO_3^- ions, or NH_4^+ and NO_3^- ions, that diffused downwards. The quantity of bromide and ammonium was estimated volumetrically.

The accuracy of the diffusion measurements depends mostly on the accuracy of the estimation of these ions in small quantities. The quantities of bromide could be determined to within 1 % error. For ease of manipulation the loss of ammonium from the upper solution was determined by difference. The results obtained in this way are less accurate than was expected. The results for ammonium ions are, nevertheless, given in the Tables to show the order of magnitude of the values obtained.

Results

The values of the diffusion coefficients for bromide and ammonium ions are recorded in Table I.

TABLE I.

DIFFUSION COEFFICIENTS FOR Br^- AND NH_4^+

Temperature ° C.	A cm.²	f	τ days	q/C_0 for bromide cc.	D_{Br^-} cm.²/day	q/C_0 for ammonium cc.	$D_{NH_4^+}$ cm.²/day
21·0 ± 0·1	6·16	0·297	2·0	3·08	1·87	—	—
21·0 ± 0·1	4·45	0·292	1·684	2·00	1·85	—	—
20·5 ± 0·1	3·79	0·303	1·670	1·696	1·74	1·54	1·44
20·5 ± 0·1	4·16	0·283	1·760	1·846	1·81	—	—
21·0 ± 0·1	3·79	0·309	1·740	1·817	1·86	1·53	1·37
21·0 ± 0·1	3·94	0·285	1·573	1·687	1·86	1·56	1·59
15·5 ± 0·25	4·14	0·284	1·750	1·691	1·53	—	—
15·5 ± 0·25	4·48	0·303	1·729	1·872	1·47	—	—
15·5 ± 0·25	3·79	0·313	1·674	1·571	1·43	1·46	1·22

The results for 15·5° c. were obtained during a period when the electric current was not available for operating the thermostat, and are consequently less accurate than those at 21·0° c., or 20·5° c.

The same technique was used to study the ionic diffusion in glistening dew, in mixtures of glistening dew and glass beads, in sand and in clays. In these experiments, the diffusion coefficients were taken from Table I, and the fractional areas were calculated. The "glistening dew" consists of glass spheres mostly of 70 I.M.M. in size, while the sand was about 200 I.M.M. in size. By mixing beads of 3·0 mm. diam. with the glistening dew, a porosity as low as 0·23 was obtained.

In addition to the inert materials of more-or-less uniform size, three different clays—kaolin, Rothamsted subsoil clay and bentonite—were studied. The kaolin, marked "Osmo No. 1 purified by electrosmosis," was supplied by Messrs. Fullers' Earth Union Limited. It contains 8 % mica. The Rothamsted subsoil clay is the clay fraction treated for the removal of iron oxide. The bentonite used was the finest fraction obtained in a supercentrifuge, with a particle size of the order of 50 millimicrons.

In order to check the values of f obtained from ionic diffusion, measurements were made of the electrical conductivities of the same systems using N./10 KBr as electrolyte. A conductivity cell with parallel rectangular electrodes, coated with platinum black, was used. Except with kaolin it was possible to obtain the porosities within the ranges used in the diffusion experiments. The kaolin suspension, however, was too thick to flow into the conductivity cell.

TABLE II.

FRACTIONAL AREAS CALCULATED FROM DIFFUSION AND CONDUCTIVITY MEASUREMENTS IN INERT MATERIALS AND CLAYS

Material	Diffusion Measurements				Conductivity Measurements	
	No. of experiments made	f_{Br^-}	$f_{NH_4^+}$	Porosity p	Porosity p	$f_{cond.}$
Glistening dew . . .	6	0·289	0·327	0·366	0·367	0·290
Glistening dew and glass beads	2	0·179	—	0·236	—	—
Sand	2	0·273	0·291	0·352	0·352	0·269
Bentonite	4	0·808	0·970	0·996	0·996	0·836
Rothamsted subsoil clay .	4	0·790	—	0·909	0·909	0·790
Kaolin	4	0·462	—	0·716	—	—

The results obtained from the diffusion and conductivity measurements are given in Table II. Although several diffusion measurements were made with each system studied, only one representative observation is recorded for each. The fractional areas were calculated from the diffusion measurements of both the Br^- and NH_4^+ ions. The ratio between the conductivity of the porous system and the free electrolyte is taken as the fractional area, $f_{cond.}$

Discussion

For a bed of coarse particles there is no doubt that the ratio f/p is simply an indication of the twists and constrictions in the water channels. The ratios obtained from Table II for the kaolin and subsoil clay are also readily interpreted in this way. The 0·91 % suspension of bentonite in N./10 KBr is a thixotropic gel, and has a conductivity 16 % less than that of the salt solution. The particles, although they occupy only 0·4 % of the total volume, consist of plates only 10 A. thick. Their thickness was established by measuring negative adsorption of chloride, which showed the total area of a gram of particles to be close to 800 sq. m. The weak rigidity of the gel and the hindrance to ionic migration could both be due to the existence of a network in which the particles tend to adhere by their edges.

In solutions containing N./40 KBr, or less, the bentonite is deflocculated, and the suspension exhibits no rigidity. Measurements of electrical conductivity, set out in Table III, show that adding the bentonite to these solutions produces a net increase of about 3 % in the conductivity. Evidently the positive contribution made by the electrophoresis of the negatively charged particles and the opposite migration of the corresponding excess of cations more than offsets the obstruction caused by the bentonite particles when they are separated from one another.

TABLE III.

RELATIVE CONDUCTIVITY OF BENTONITE SUSPENSIONS IN POTASSIUM BROMIDE SOLUTIONS AT DIFFERENT CONCENTRATIONS

Normality of Electrolyte	Per cent. Weight of Bentonite	Relative Conductivity
0·1	0·91	0·836
0·05	1·14	0·924
0·0333	0·76	0·971
0·025	0·57	1·028
0·0167	0·38	1·026
0·0125	0·27	1·037
0·0083	0·19	1·033

In Table II it will be seen that $f_{\text{cond.}}$ for the bentonite suspension is 0·836 while f_{Br^-} is only 0·808. We believe this difference to be outside experimental error, and to be due to the excess of cations balancing the negative charges on the particles. The kaolin and the subsoil clay also give rise to additional conductance that can be observed in very dilute salt solutions, but which would not give rise to significant differences in Table II. We should expect $f_{\text{cond.}}$ to be roughly the mean of f_{Br^-} and $f_{NH_4^+}$. The measurements with ammonium were not, however, precise enough to test this.

The low ionic migration in the suspensions of bentonite in N./10 KBr when first observed seemed to point to an increase in the viscosity of the water. When, however, no such effect was apparent in N./40 KBr this idea was abandoned. It is hardly conceivable that a drastic change in the viscosity of water could occur in the stronger, but not in the weaker, salt solution. We therefore see no escape from the conclusion that this bentonite reduces the conductivity of N./10 KBr mainly by a process of obstruction due to the manner in which the particles are linked in the thixotropic gel. Consequently we consider that these studies of ionic migration give powerful support to the view that the particles of this thixotropic gel, though not in actual solid contact, form a kind of network in which the edges of neighbouring particles are drawn towards each other.

NOTE ADDDED IN PROOF:

The drag restraining the diffusion of the bromide ion is given by kT/D, and works out at $1·9 \times 10^{-9}$ dyne sec. cm.$^{-1}$, taking D as 1·86 cm.^{2}/day in N./10 KBr. at 21° C. The drag in electrolytic conduction is e/u, and works out at $2·45 \times 10^{-9}$ dyne sec. cm.$^{-1}$ taking the mobility, u, of the bromide ion in N./10 KBr at 21° C. as $6·55 \times 10^{-4}$ cm.^{2} sec.$^{-1}$ volt^{-1}. Taking the mobility at infinite dilution as $7·47 \times 10^{-4}$, the corresponding drag is $2·15 \times 10^{-9}$. Thus it appears that the drag against random Brownian movement is slightly less than the drag at infinite dilution calculated from conductivity measurements. We are examining the theory of the ionic atmosphere to see whether it can throw light on the effect we have observed.

Summary

A technique has been developed for measuring separately the diffusion coefficients of the cations and anions of a salt solution. Knowing these coefficients, measurements of ionic diffusion give the effective fraction area of the water channels in porous systems ranging from glass beads through sands to fine clays.

In the clay systems there are more cations than anions owing to the negative charges on the particles. Taking this into consideration, the electrical conductivities are found to be concordant with the diffusion measurements.

The conductivity of N./10 KBr solution is reduced 16 % by adding 0·91 % of a very fine bentonite which, under these conditions, forms a thixotropic gel, whereas the conductivity of N./40 KBr is increased 3 % by adding 0·57 % of the same bentonite which in this case forms a deflocculated suspension devoid of rigidity. These bentonite particles are plates 10 A. thick.

These results strongly support the view that the bentonite particles in a thixotropic gel form a kind of network in which the edges of neighbouring particles are drawn towards each other.

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FLUID FLOW IN POROUS MEDIA

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(1) Introduction

There are various ways in which a fluid such as water may be transported in a porous medium. The transport mechanisms depend upon pressure, physical state of the fluid (gas or liquid), the nature of the capillaries (their diameter, length, shape, roughness and regularity), the temperature, the isothermal or adiabatic condition of flow, and sometimes upon surface tension. It is convenient, as will be done in this paper, to classify the flow processes according to the nature of the fluid. Thus one has:

(i) transport of incompressible fluids and displacement of one fluid by another,
(ii) transport of compressible fluids, such as may occur inside the earth under great pressures,
(iii) transport of gases and vapours.

Clearly, water may behave as any one of the above fluids according to conditions of temperature and pressure. One may employ a general relation[1 2] between pressure p and fluid density d to cover the fluid in all three of the above conditions:

$$d = d_0 \, p^m \, e^{\beta p} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where for incompressible fluids, $m = \beta = 0$; for compressible fluids $m = 0$, $\beta \neq 0$; and for gases $\beta = 0$ and $m = 1$ in isothermal flow systems and $\beta = 0$, $m = \dfrac{C_v}{C_p}$ in adiabatic flow systems. C_v and C_p are as usual the heat capacities at constant volume and pressure respectively.

(2) Displacement of One Liquid by Another

At least one of the fluids will be considered as incompressible, and their mutual interface assumed to make an angle θ with the wall of a capillary of radius r and length l (Fig. 1). The axis of the capillary is inclined at an angle φ to the vertical. One may normally neglect inertial effects and kinetic energy of flow and in the steady state, when one liquid of density d_1

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[1] Hurst, *Physics*, 1934, 5, 20.
[2] Muskat, *Physics*, 1934, 5, 71.

has displaced the other of density d_2 a distance x up the tube, one has

$$\Delta P\pi r^2 + 2\pi r\sigma_{12}\cos\theta = 8\pi\eta_1 x\frac{dx}{dt} + 8\pi\eta_2(l-x)\frac{dx}{dt}$$
$$+ \pi r^2 g\{d_1x - d_2(l-x)\}\sin\varphi \quad . \quad . \quad . \quad (2)$$

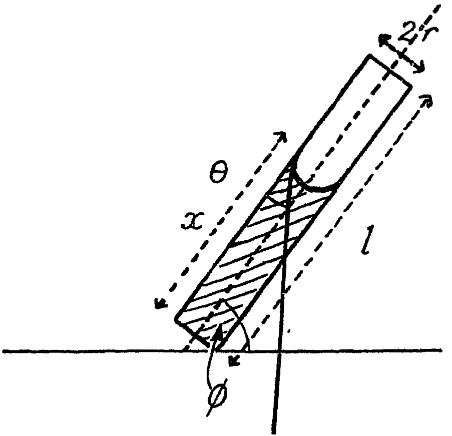

Fig. 1.

This equation is seen to denote a balance between hydrostatic and surface-tension forces on the one hand, and viscous and gravitational forces on the other. In eqn. (2) terms not so far designated are:

ΔP = pressure difference between the ends of the tube,

σ_{12} = the interfacial tension between the liquids,

η_1, η_2 = the viscosities of the fluids,

$\frac{dx}{dt}$ = the velocity of the interface.

On rearranging this equation one obtains for the volume of liquid leaving or entering the capillary in unit time:

$$\pi r^2\frac{dx}{dt} = \frac{dv}{dt} = \frac{\pi r^4[\Delta P - g\{d_1x - d_2(l-x)\}\sin\varphi] + 2\pi r^3\sigma_{12}\cos\theta}{8\eta_1 x + 8\eta_2(l-x)} \quad (3)$$

For a horizontal tube when $\Delta P = 0$,

$$\frac{dv}{dt} = \frac{\pi r^3\sigma_{12}\cos\theta}{4\{\eta_1 x + \eta_2(l-x)\}} \quad . \quad . \quad . \quad (4)$$

while if the displaced fluid is air the term in η_2 can be omitted from (4). Tests of the laws of horizontal displacement under surface-tension forces only have shown reasonable agreement taking θ to be that for a static system.[8]

When gravitational and surface-tension forces are negligible,

$$\frac{dv}{dt} = \frac{\Delta P\pi r^4}{8\eta_1 x + 8\eta_2(l-x)} \quad . \quad . \quad . \quad (5)$$

which reduces to a standard hydrodynamic formula when $x = l$. Also when $\Delta P \sim 1$ atm., examination of eqn. (3) shows that the contribution to flow due to surface tension becomes comparable with, or greater than, the hydrostatic contribution when $r \lesssim 10^{-4}$ cm. Thereafter the liquid will move *against* considerable hydrostatic pressure if $\cos\theta$ is negative $(\frac{\pi}{2} < \theta < \pi)$ (Fig. 2). Reekie and Aird [8a] have in this connection shown that when $r \sim 10^{-5}$ cm. an air pressure of at least 3 atm. will not displace water from the capillary system.

The angle θ may under flow conditions deviate from its value for a static system. A meniscus which normally corresponds to Fig. 2 (*a*) may at higher

[8] Eley and Pepper, *Trans. Faraday Soc.*, 1946, **42**, 697.
[8a] Reekie and Aird, *Nature*, 1945, **156**, 367.

velocity under pressure take the form of Fig. 2 (*b*), and the surface-tension contribution to flow will then become artificially reversed.

An accurate generalisation of eqn. (3) to porous media is difficult, but an approximation is to regard the network as a bundle of N parallel capillaries, all of mean radius r and of length $k_1 l$ where k_1 is a tortuosity factor.[8] Such an extension does not allow for cross-connection of capillaries or for diameters which vary along their length ; nor does it deal with non-circular cross-sections. However, the total flow now is:

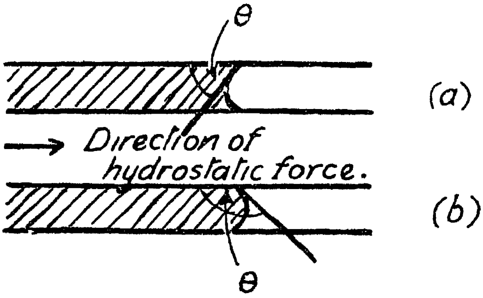

FIG. 2.

$$N\frac{\mathrm{d}v}{\mathrm{d}t}=N\left\{\frac{\pi r^4[\Delta P-gk_1\{d_1x-d_2(l-x)\}\sin\varphi]+2\pi r^3\sigma_{12}\cos\theta}{8\,k_1^2\eta_1x+8\,k_1^2\eta_2(l-x)}\right\}\quad . \quad (6)$$

(3) Flow of Compressible Fluids

For a compressible fluid where the relation between density d and external pressure p is $d=d_0e^{\beta p}$ (cp. Section 1), the equation of flow in the transient state is [2]

$$\frac{\partial d}{\partial t}=\frac{k_2}{\varepsilon\beta\eta}\nabla^2 d\quad . \quad . \quad . \quad . \quad . \quad (7)$$

where ε denotes the porosity and k_2 is a constant called by some workers the "permeability" (see footnote, p. 64). In the steady state $\frac{\partial d}{\partial t}=0$, and therefore one finds for density and pressure distributions:

$$\left.\begin{aligned} d&=-(d_2-d_1)\frac{x}{l}+d_2\\ p&=\frac{1}{\beta}\ln\left\{-(d_2-d_1)\frac{x}{l}+d_2\right\}-\frac{1}{\beta}\ln d_0\end{aligned}\right\}\quad . \quad . \quad (8)$$

This means that the mass rate of flow of fluid, $Q=d\times\frac{\mathrm{d}v}{\mathrm{d}t}$, in the steady state is

$$Q=\frac{k_2(d_2-d_1)}{\beta\eta l}=\frac{k_2d_0}{\beta\eta l}\left\{\exp(\beta p_2)-\exp(\beta p_1)\right\}\quad . \quad . \quad (9)$$

In these equations, d_1, d_2 and p_1, p_2 are densities and pressures at the two ends of the tube. On expanding the exponentials, and for small values of β, taking only terms up to and inclusive of β^2, one has

$$Q=Q_0\left(1+\frac{\beta(p_1+p_2)}{2}\right)\quad . \quad . \quad . \quad . \quad (10)$$

where Q_0 is the mass rate of flow for an incompressible fluid. This we know from Section 2 is $\frac{d_0(p_1-p_2)\pi r^4}{8\eta l}$ for a single capillary, while for a porous bed it is $\frac{k_2 d_0}{\eta l} \cdot (p_1 - p_2)$.* Eqn. (10) shows that other things being equal, the volume flow is greater for a compressible than for an incompressible fluid.

There is an important application of eqn. (7) to subterranean fluid flow as in artesian water or oil reservoirs. On opening a well the pressure at the well bore is released in part so that the fluid near the bore and the rock expand slightly, and the pressure gradient thereby established ($d = d_0 e^{\beta p}$) drives the fluid to the well. As fluid is removed by this drive the pressure falls progressively at more and more distant points. Usually the oil- and water-bearing strata are comparatively thin but of great lateral extent, so that the problem is best considered as one of cylinder flow. The enormous quantities of liquid in the fluid-bearing strata permit extraction of great quantities of fluid due simply to its volumetric expansion and to the volumetric expansion of the rock substance on pressure release, slight though these may be per unit volume. The eqn. (7) is more correctly rewritten as $\frac{\partial d}{\partial t} = \frac{k_2}{\varepsilon\beta_l + \beta_m} \nabla^2 d$ where β_l is the fluid compressibility and β_m that of the rock substance.[35] However, this is identical with (7) if $\beta = \left(\beta_l + \frac{\beta_m}{\varepsilon}\right)$. It is also to be noted that strictly ε is a function of pressure, so that eqn. (7) is non-linear but this introduces only a small effect and is neglected.

In one possible case one may have *density* (or pressure) at the inner and outer boundaries of the oil-bearing region as functions of time. Expressed analytically:

$$\begin{aligned} d &= f_1(t) \text{ at } r = r_1 \\ d &= f_2(t) \text{ at } r = r_2 \\ d &= f(r) \text{ at } t = 0 \text{ for } r_1 < r < r_2 \end{aligned}$$

The solution now is:

$$d = \pi \sum \frac{\alpha_n^2 J_0(\alpha_n r_1)\, U(\alpha_n r)}{J_0^2(\alpha_n r_1) - J_0^2(\alpha_n r_2)} e^{-D\alpha_n^2 t} \left[\frac{\pi}{2} J_0(\alpha_n r_1) \int_{r_1}^{r_2} r \; f(r)\, U(\alpha_n r)\, dr \right.$$

$$\left. - D J_0(\alpha_n r_2) \int_0^t f_1(\lambda) e^{D\alpha_n^2 \lambda}\, d\lambda + D\, J_0(\alpha_n r_1) \int_0^t f_2(\lambda) e^{D\alpha_n^2 \lambda}\, d\lambda \right] \quad . \qquad (11)$$

where
$$D = \frac{k_2}{\varepsilon\beta\eta};$$

$$U(\alpha_n r) = Y_0(\alpha_n r_2) J_0(\alpha_n r) - J_0(\alpha_n r_2) Y_0(\alpha_n r);$$

α_n = the n^{th} positive root of $U(\alpha_n r_1) = 0$, and J_0 and Y_0 denote Bessel functions of zero order and the first and second kind respectively. One may identify r_2 with an outer radius of the oil-bearing region, and r_1 with the well radius.

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[35] Shchelkachov, *Compt. rend., U.R.S.S.*, 1946, **52**, 103; *Compt. rend., U.R.S.S.*, 1946, **52**, 395.

* The "permeability" k_2 defined by eqn. (7) is $\frac{N\pi r^4}{8k_1^2}$ if the system is idealised as N parallel capillaries, each of mean length $k_1 l$ and mean radius r. k_1 as in Section 2 allows for the tortuosity of the capillaries. More precisely, the expression for k_2 should be $\sum_r \frac{\pi r^4}{8k_1^2 l}$ See also Section 4, p. 67.

In a second case the *flux* at one boundary and the *density* at the other are functions of time:

$$d = \mathrm{f}_1(t) \text{ at } r = r_1$$
$$r\frac{\partial d}{\partial r} = \mathrm{f}_2(t) \text{ at } r = r_2$$
$$d = \mathrm{f}(r) \text{ for } r_1 < r < r_2 \text{ at } t = 0$$

The solution now is

$$d = \pi \sum \frac{a_n^2 \mathrm{J}_0(a_n r_1)\mathrm{U}(a_n r)}{\mathrm{J}_0^2(a_n r_1) - \mathrm{J}_1^2(a_n r_2)} e^{-D\alpha_n^2 t} \left[\frac{\pi}{2} \mathrm{J}_0(a_n r_1) \int_{r_1}^{r_2} r \, \mathrm{f}(r)\mathrm{U}(a_n r)\mathrm{d}r \right.$$
$$\left. - D\mathrm{J}_1(\alpha_n r_2) \int_0^t \mathrm{f}_1(\lambda) e^{D\alpha_n^2 \lambda} \, d\lambda - \frac{D\mathrm{J}_0(a_n r_1)}{a_n r_2} \int_0^t \mathrm{f}_2(\lambda) e^{D\alpha_n^2 \lambda} \, \mathrm{d}\lambda \right] \quad . \quad (12)$$

where $\mathrm{U}(a_n r) = \mathrm{Y}_1(a_n r_2)\,\mathrm{J}_1(a_n r) - \mathrm{J}_1(a_n r_2)\,\mathrm{Y}_0(a_n r)$, a_n is the n^{th} positive root of $\mathrm{U}(a_n r_1) = 0$, and J_1, Y_1, are Bessel functions of the first order and first and second kind respectively.

Finally, the *flux* at both boundaries is taken as a function of time,

$$r\frac{\partial d}{\partial r} = \mathrm{f}_2(t) \text{ at } r = r_2$$
$$r\frac{\partial d}{\partial r} = \mathrm{f}_1(t) \text{ at } r = r_1$$
$$d = \mathrm{f}(r) \text{ for } r_1 < r < r_2 \text{ at } t = 0,$$

a set of conditions giving as solution:

$$d = \frac{2D}{r_2^2 - r_1^2} \int_0^t \left\{ \mathrm{f}_2(\lambda) - \mathrm{f}_1(\lambda) \right\} \mathrm{d}\lambda + \frac{2}{r_2^2 - r_1^2} \int_{r_1}^{r_2} r \, \mathrm{f}(r)\mathrm{d}r$$
$$+ \pi \sum \frac{a_n^2 \mathrm{J}_1(a_n r_1)\mathrm{U}(a_n r)}{\mathrm{J}_1^2(a_n r_1) - \mathrm{J}_1^2(a_n r_2)} e^{-D\alpha_n^2 t} \left[\frac{\pi}{2} \mathrm{J}_1(a_n r_1) \int_{r_1}^{r_2} r \, \mathrm{f}(r)\mathrm{U}(a_n r)\mathrm{d}r \right.$$
$$\left. + \frac{D\,\mathrm{J}_1(a_n r_2)}{a_n r_1} \int_0^t \mathrm{f}_1(\lambda) e^{D\alpha_n^2 \lambda} \, \mathrm{d}\lambda - \frac{D\,\mathrm{J}_1(a_n r_1)}{a_n r_2} \int_0^t \mathrm{f}_2(\lambda) e^{D\alpha_n^2 \lambda} \, \mathrm{d}\lambda \right] \quad . \quad (13)$$

where $\mathrm{U}(a_n r) = \mathrm{Y}_1(a_n r_2)\mathrm{J}_1(a_n r) - \mathrm{J}_1(a_n r_2)\mathrm{Y}_1(a_n r)$, and α_n is the n^{th} positive root of $\mathrm{U}(\alpha_n r_1) = 0$.

From the general equations (11), (12) and (13) one may readily write down the solutions for particular values of $\mathrm{f}_1(t)$, $\mathrm{f}_2(t)$ and $\mathrm{f}(r)$. The solutions (11), (12) and (13) cover all probable conditions governing the release of oil or artesian water. For their numerical application, which leads to reasonable values for pressure-decline and oil-yield in typical fields, the papers of Muskat,[2] Hurst,[1] or Shchelkachov[3b] may be consulted.

If the porous medium is charged not with oil but with gas, on opening the field the yield of gas may be expected to follow the transient-state equation for isothermal flow *

$$\frac{\partial d}{\partial t} = \frac{k_2}{2\eta d_0} \nabla^2 (d^2) \quad . \quad . \quad . \quad . \quad (14)$$

which is seen to be non-linear, so that exact solutions cannot be obtained. Approximate methods are still available, which will not, however, be discussed here.

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* The relation between density and pressure for the gas is $d = d_0 p$ where d_0 is seen to be the density when $p = 1$.

TABLE I

SOME FLOW MECHANISMS IN CAPILLARIES.*

Process	Formula for Flow
(1) Effusion of molecules through an orifice of area A in a thin wall.	$\frac{dn}{dt} = \frac{Ap}{\sqrt{2\pi mkT}}$ $p_1v_1 = Ap_1\sqrt{\frac{kT}{2\pi m}}$
(2) Molecular streaming or Knudsen flow in capillaries (mean-free-path>capillary diameter).	$\frac{dn}{dt} = \frac{\frac{1}{2}B}{\sqrt{2\pi mk}}\left(\frac{p_1}{\sqrt{T_1}} - \frac{p_2}{\sqrt{T_2}}\right)\frac{1}{l}\cdot\frac{2-f}{f}$ $= \frac{8}{3}\frac{\pi r^3}{\sqrt{2\pi mk}}\left(\frac{p_1}{\sqrt{T_1}} - \frac{p_2}{\sqrt{T_2}}\right)\frac{1}{l}\cdot\frac{2-f}{f}$ (for capillary of circular cross-section).
(3) Isothermal streamline or Poiseuille flow (mean-free-path<capillary diameter).	$\frac{dn}{dt} = \frac{\pi r^4}{8l\eta}\cdot\frac{1}{kT}\cdot\frac{p_1^2 - p_2^2}{2}$ $p_1v_1 = \frac{\pi r^4}{8l\eta}\cdot\frac{p_1^2 - p_2^2}{2}$ (for capillary of circular cross-section).
(4) Combined Poiseuille and Knudsen flow, with allowance for fraction of pressure difference producing energy of motion.	$\frac{dn}{dt} = \frac{1}{8l\eta}\left(1 + \frac{4(2-f)}{f}\cdot\frac{\lambda}{r}\right)$ $\left\{\frac{\pi r^4}{kT}\cdot\frac{p_1^2 - p_2^2}{2} - \frac{m}{\pi}\left(\frac{dn}{dt}\right)^2\right\}$
(5) Adiabatic stream-line flow (mean-free-path <capillary diameter).	$\left(\frac{dn}{dt}\right)_{\text{adiabatic}} =$ $\left(\frac{dn}{dt}\right)_{\text{isothermal}} \times \frac{2}{(1+\gamma)}\cdot\left(\frac{1 - \left(\frac{p_1}{p_2}\right)^{1+\gamma}}{1 - \left(\frac{p_1}{p_2}\right)^2}\right)$
(6) Adiabatic or orifice flow through a short frictionless jet of cross-section A_1 at its nozzle, and nozzle radius r.	$v_2 = A_1\sqrt{2T_1C_p\left\{1 - \left(\frac{p_2}{p_1}\right)^{\frac{\gamma-1}{\gamma}}\right\}}$ $v =$ $(\pi r^2)\sqrt{2T_1C_p\cdot\left(\frac{p_2}{p_1}\right)^{2/\gamma}\left\{1 - \left(\frac{p_2}{p_1}\right)^{\frac{\gamma-1}{\gamma}}\right\}}$
(7) Turbulent high-pressure flow.	$(p_1v_1)^2 = (p_2v_2)^2$ $= \frac{\pi^2 r_h r^4}{\xi l}(p_1^2 - p_2^2)$

* Terms in Table I not already defined are in order of occurrence:

$\frac{dn}{dt}$ = rate of flow in molecules/sec.
N_0 = Avogadro number.
v_1 = the volume flowing/sec. measured at pressure p_1.
k = Boltzmann's constant.
m = the mass of a molecule.
B = a shape factor.
T_1, T_2; p_1, p_2 = temperatures and pressures at the two ends of a tube.
f = the fraction of molecules striking the wall which are re-emitted at random.
$(1 - f)$ = the fraction of molecules striking the wall which are specularly reflected.
λ = the mean-free-path.
γ = the ratio of the two heat capacities, $\frac{C_p}{C_v}$.
v_2 = the volume leaving the orifice measured at the outgoing pressure p_2.
v = the volume leaving the orifice reduced to the pressure p_1 at the ingoing side of the orifice.
r_h = the hydraulic radius $-\frac{\text{cross-section}}{\text{circumference}}$
an empirical factor depending *inter alia* upon roughness and other properties of the tube.

(4) Flow of Gas and Vapour

(a) Steady States of Flow. One may first consider flow in the steady state in single capillaries. Various processes which are possible are summarised in Table I.[4] These flow mechanisms have been especially examined in molecular streaming or Knudsen, and in higher pressure or Poiseuille, ranges by Knudsen,[5] Clausing,[6] Warburg [7] and others.[8, 9, 10] For single capillaries they have been comparatively well substantiated.

Adiabatic flow processes [11, 2, 12] have also received attention, although experimental conditions for their occurrence are less easily realised, except perhaps for orifice flow. The latter may be expected in transmission of gases and vapours through textile fabrics. Papers and fibre-boards have been studied in the same connection; the results have, however, proved more nearly in conformity with Poiseuille's law except for the thinnest membranes where transmission may have been intermediate between orifice and Poiseuille flow. Certain aspects of the behaviour do not accord with either mechanism, but may be ascribed to the compressibility of the membranes.[12]

Practical applications of low-pressure flow arise in design and theory of high vacuum pumps,[13] molecular stills,[14] and in isotope separation.[4, 15] At the high-pressure end, engineering applications to the theory of turbines, aerodynamics and jet propulsion fall outside the scope of the present review. One may confine discussion to some information concerning porous solids obtainable in the molecular streaming or streamline flow regions.

One such application consists in determining the specific area of powders from permeability measurements. Following the work of Kozeny,[16] Carman [17] and most recently Rigden [18] have, among others,[19, 20, 21] developed the theory. Rigden [18] allowed for "slip" at the pore wall, corresponding to overlap of streamline flow and molecular streaming, by introducing a correction term $\left(1+\frac{4\lambda x}{r}\right)$ as multiplier of the usual equation (Table I, No. 3). Taking $x = 0{\cdot}874$, Rigden found that his corrected equation gave an unusually satisfactory agreement between specific surfaces determined by air and liquid permeability measurements. The term $\left(1'+\frac{4\lambda x}{r}\right)$ is equivalent to the term $\left(1+\frac{4(2-f)\lambda}{fr}\right)$ in Table I, No. 4, but the chosen value of x makes $f > 1$.* The Kozeny method is considered elsewhere in this symposium, and will not be discussed here.

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[4] Cp. Barrer, *Diffusion in and Through Solids* (C.U.P., 1941), Ch. 2.

[5] Knudsen, *Ann. Physik.*, 1909, **28**, 75; 1911, **35**, 389.

[6] Clausing, *Ann. Physik.*, 1930, **7**, 489, 569.

[7] Warburg, *Ann. Physik.*, 1876, **159**, 399.

[8] Gaede, *Ann. Physik.*, 1913, **41**, 289.

[9] Smoluchowski, *Ann. Physik.*, 1910, **33**, 1559.

[10] Klose, *Physik. Z.*, 1930, **31**, 503; *Ann. Physik.*, 1931, **11**, 73.

[11] Buckingham, *U.S. Bur. Stand.*, Tech. Paper No. 183, 1921.

[12] Carson, *Bur. Stand. J. Res.*, 1934, **12**, 587.

[13] Avery and Witty, *Proc. Phys. Soc. A*, 1947, **59**, 1016.

[14] Hickman, *Chem. Rev.*, 1944, **34**, 51.

[15] e.g., *Ann. Reports*, 1938, **35**, 138.

[16] Kozeny, *Ber. Wien. Akad.*, 1927, **136a**, 271.

[17] Carman, *J. Soc. Chem. Ind.*, 1938, **57**, 225; *J. Soc. Chem. Ind.*, 1939, **58**, 1; *Trans. Inst. Chem. Eng.*, 1937, **15**, 150; *J. Agric. Sci.*, 1939, **29** (2), 262.

[18] Rigden, *J. Soc. Chem. Ind.*, 1943, **62**, 1; *J. Soc. Chem. Ind.*, 1947, **66**, 130.

[19] Muskat, *The Flow of Homogeneous Liquids Through Porous Media* (1937); *Physics*, 1932, **2**, 329.

[20] Lea and Nurse, *J. Soc. Chem. Ind.*, 1939, **58**, 277.

[21] Gooden and Smith, *Ind. Eng. Chem.* (*Anal.*), 1940, **12**, 479.

Another useful but less well-known approach to the properties of porous solids also depends on overlap of streamline flow with molecular streaming.[22] Writing the Poiseuille law as $G_P = \frac{a(p_1^2 - p_2^2)}{2}$ and the Knudsen law as $G_K = b(p_1 - p_2)$, one may write for the overall flow

$$G = G_P + \alpha G_K = K(p_1 - p_2) \quad . \quad . \quad . \quad (15)$$

where α is a constant depending on "slip." Thus

$$K = \frac{A_1 r^4}{l} \cdot \frac{p_1 + p_2}{2} + \frac{\alpha B_1 r^3}{l} \quad . \quad . \quad (16)$$

and comparison with Table 1, No. 4, gives for a circular tube

$$A_1 = \frac{\pi}{8\eta} \; ; \; \alpha B_1 = \frac{3\pi^2}{4}\sqrt{\frac{kT}{2\pi m}} \cdot \frac{2-f}{f} \simeq \frac{3\pi^2}{4}\sqrt{\frac{kT}{2\pi m}}$$

(as noted below, the actual numerical magnitude of B_1 may need slight adjusting). Next, for N capillaries of radius r in parallel one has

$$G = K'(p_1 - p_2) \quad . \quad . \quad . \quad . \quad (17)$$

with

$$K' = K_1 + K_2 + \ldots\ldots = A_1\left(\frac{p_1 + p_2}{2}\right)\sum^{N}\frac{r^4}{l} + \alpha B_1\sum^{N}\frac{r^3}{l} \quad . \quad (18)$$

Again, when there are two capillaries of radii r_1 and r_2 and lengths l_1 and l_2 joined in series one has for the overall flow

$$G = K''(p_1 - p_2) \quad . \quad . \quad . \quad . \quad (19)$$

and for the sections of lengths l_1 and l_2

$$\left.\begin{aligned} G_1 &= G_{1P} + \alpha G_{1K} = K_1(p_1 - p_0) \\ G_2 &= G_{2P} + \alpha G_{2K} = K_2(p_0 - p_2) \end{aligned}\right\} \quad . \quad . \quad (20)$$

and in the steady state $G = G_1 = G_2$; p_0 here denotes the pressure at the junction point between the two sections. Denoting $\frac{p_0 - p_2}{p_1 - p_0}$ by R, then from $G = G_1$, on rearranging one has

$$\frac{1}{K_1}(1 + R) = \frac{1}{K''} \quad . \quad . \quad . \quad . \quad (21)$$

From $G = G_2$, one obtains similarly

$$\frac{1}{K_2}\left(\frac{1}{R} + 1\right) = \frac{1}{K''} \quad . \quad . \quad . \quad . \quad (22)$$

Adding these relations, dividing by two and rearranging further, gives

$$\frac{1}{K''} = \frac{1}{K_1} + \frac{1}{K_2} + \left\{\frac{1}{2}\;\frac{1}{K_1}(R - 1) - \frac{1}{2}\frac{1}{K_2}\frac{(R-1)}{R}\right\} \quad . \quad (23)$$

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* f denoting the fraction of molecules striking the wall which are randomly re-emitted, cannot be greater than unity. However, there is uncertainty as to the correct theoretical numerical factor for "slip" (cp. [23]), and as to the way the factor may be modified by roughness of the capillary wall.

[22] Adzumi, *Bull. Chem. Soc., Japan*, 1937, 12, 304.

But from the relation $G_1 = G_2$ one finds $K_1 = K_2R$ so that the term in the bracket is zero, and

$$K'' = \frac{1}{\frac{1}{K_1} + \frac{1}{K_2}} \quad . \quad . \quad . \quad . \quad . \quad (24)$$

This expression Adzumi [22] reduced to

$$K'' = \frac{A_1(p_1 + p_2)}{2}\left(\frac{l_1}{r_1^4} + \frac{l_2}{r_2^4}\right)^{-1} + aB_1\left(\frac{l_1}{r_1^3} + \frac{l_2}{r_2^3}\right)^{-1} + \delta \ . \quad (25)$$

where the correction term δ was small. Generalising for a composite capillary comprising m capillaries joined in series, he gave:

$$K'' = \frac{A_1(p_1 + p_2)}{2}\frac{1}{\sum^{m}\frac{l}{r^4}} + \frac{aB_1}{\sum^{m}\frac{l}{r^3}} \quad . \quad . \quad . \quad (26)$$

Idealising the porous solid as a combination series-parallel arrangement of capillaries, one then obtains for the final flow " constant ":

$$K = A_1\frac{p_1 + p_2}{2}\sum^{N}\left(\frac{1}{\sum^{m}\frac{l}{r^4}}\right) + aB_1\sum^{N}\left(\frac{1}{\sum^{m}\frac{l}{r^3}}\right) \quad . \quad . \quad (27)$$

$$= A_1E\left(\frac{p_1 + p_2}{2}\right) + aB_1F \quad . \quad . \quad . \quad (28)$$

where E and F are the double summations above. If, therefore, one measures the flow rate, say in cc. per unit time at 1 atm., this rate divided by $(p_1 - p_2)$ should be a linear function of the mean pressure and the slope of this line will fix A_1E while its intercept will determine aB_1F. The equation would appear from Fig. 3 to give a reasonable representation of observational data.

Regarding all the capillaries as having the mean radius $\bar{r}$ and mean length l, one has $E = \frac{N\bar{r}^4}{l}$; $F = \frac{N\bar{r}^3}{l}$, and knowing the values of A_1 and aB_1 (see p. 68) one can, from the slope and intercept of the curves of Fig. 3, determine both E and F, and so find both N and $\bar{r}$. This also permits an estimate of the internal surface of the solid. Table II gives the relevant data for several porous membranes.

Such an estimate can only be a lower limit to this area, however, since, as in the Kozeny method, the roughness of the internal surface is not easily allowed for, and moreover N' in Table II is more properly $\frac{N'}{k_1^2}$, where k_1 is the tortuosity factor of p. 63. However, when used in conjunction with the BET isotherm

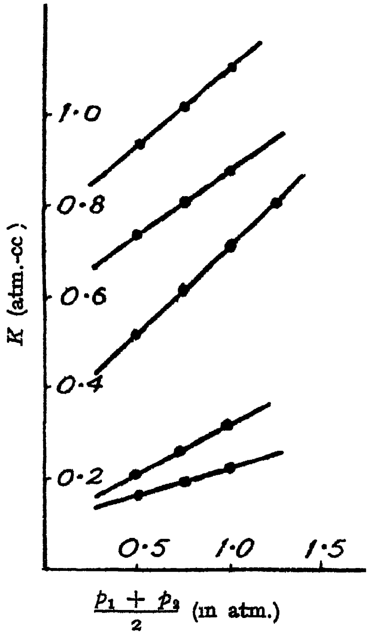

FIG. 3.—Typical examples of gas flow through porous plates, after Adzumi, in test of the equation: $K = A_1E\frac{(p_1 + p_2)}{2} + aB_1F$

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[23] Cp. Taylor, *Treatise on Physical Chemistry* (Macmillan, 1931), p. 176.

method [24] the data will give a good idea of the correction involved in roughness and tortuosity. On the other hand, no information can result as to the distribution of pore sizes. For this purpose the procedure described by Foster may be used (this discussion). Lochmann has also used Adzumi's method to determine pore size.[24a]

TABLE II

STRUCTURAL PROPERTIES ASSESSED BY A FLOW METHOD

Porous Plate	Thickness	$r \times 10^5$ (cm)	N' (Number of Pores in a cm. Cube)	Internal Surface in cm ^{2}/cc. of Solid
Unglazed earthenware .	0·15	5·3	$1{\cdot}2 \times 10^6$	333
Compact porous pot .	0·27	2 77	$9{\cdot}6 \times 10^5$	47
Rough porous pot .	0·41	4·84	$2{\cdot}8 \times 10^5$	85
Mantle of Daniell cell I .	0·2	1·61	$9{\cdot}6 \times 10^7$	9,800
Mantle of Daniell cell II .	0·2	1·71	$1{\cdot}19 \times 10^8$	13,000

(b) Transient Flow in Capillaries.—Reference has already been made to the transient state in streamline flow (p. 67). The transient state in molecular streaming (Knudsen flow) is also of interest, because treatment of Table I, No. 2, in the same way as is usual in deriving Fick's second law from the first law [25] leads directly for an isothermal system to:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$

where C is expressed in molecules/cc. and

$$D = \frac{1}{2}\frac{B}{\pi r^2}\sqrt{\frac{kT}{2\pi m}}\cdot\frac{2-f}{f} = \frac{8r}{3}\sqrt{\frac{kT}{2\pi m}}\cdot\frac{2-f}{f} \quad \text{(for a cylindrical tube).}$$

On integrating this equation for the boundary conditions,

$$\begin{gathered} C = C_1 \text{ for all } t \text{ at } x = 0 \\ C \rightharpoonup 0 \text{ for all } t \text{ at } x = l \\ C = 0 \text{ for } t = 0 \text{ and } 0 < x < l \end{gathered}$$

one has

$$C = C_1\left\{\frac{l-x}{l} - \frac{2}{\pi}\sum_{m=1}^{\infty}\frac{-(-1)^m}{m}\exp\left(-\frac{m^2\pi^2 Dt}{l^2}\right)\sin\frac{m\pi(l-x)}{l}\right\} \quad . \quad (29)$$

The number of molecules, n_2, which has streamed past the boundary at $x = l$ in time t is then

$$n_2 = \frac{DC_1}{l}\left[t - \frac{2l^2}{\pi^2 D}\left\{\left(1 - \exp\left(\frac{-\pi^2 Dt}{l^2}\right)\right) - \frac{1}{4}\left(1 - \exp\left(\frac{-4\pi^2 Dt}{l^2}\right)\right.\right.\right.$$
$$\left.\left.\left. + \frac{1}{9}\left(1 - \exp\left(\frac{-9\pi^2 Dt}{l^2}\right)\right) - \ldots\ldots\right\}\right] \quad . \quad . \quad (30)$$

which at large values of t leads to

$$n_2 = \frac{DC_1}{l}\left[t - \frac{l^2}{6D}\right] \quad . \quad . \quad . \quad . \quad (31$$

so that the intercept L made by the limiting slope of n_2 against t on the axis of t is

$$L = \frac{l^2}{6D} = \frac{l^2}{16r\sqrt{\frac{kT}{2\pi m}}\cdot\frac{(2-f)}{f}} \quad . \quad . \quad (32)$$

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[24] Brunauer, *Physical Adsorption of Gases and Vapours*, Vol. I (O U P., 1944), p. 285.

[24a] Lochmann, *Angew. Chem*, 1940, **53**, 505.

[25] Cp. ref. [4], Ch. 1.

One may take $f = 1$, i.e., all molecules striking the surface are re-emitted at random, and compute values of L for oxygen gas passing at 293° K. through a capillary 25 cm. long:

r (cm.)	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}
L (sec.)	0·036	0·36	3·6	36	360

The above time lag will, however, be increased if the lifetime of a molecule in the adsorbed state becomes appreciable compared with the time of transit across the tube. This requires the use of a corrected value of D:

$$D = \frac{4r^2}{3r \, . \sqrt{\frac{\pi m}{2kT}} + \tau} \quad . \quad . \quad . \quad (33)$$

Clearly when r is small enough, L may be considerably augmented by this immobilisation of molecules in the adsorbed state. Moreover, $\tau = \tau_0 \, e^{\frac{\Delta H}{RT}}$ where $\tau_0 = \frac{1}{\nu}$ is the reciprocal of the vibration frequency of the sorbed molecule relative to the surface and ΔH is the heat of adsorption per g. mol. Clausing [6] was able to interpret measurements on low-pressure transients in capillaries to give τ and ΔH for several molecules.

However, a further correction not considered by Clausing may be necessary if there is any surface mobility of absorbed molecules. In zeolitic channels of molecular dimensions where the diffusing species never leave the range of surface forces it has been demonstrated that diffusion of permanent gases may occur rapidly under suitable conditions.[26] [27] Similarly, therefore, surface diffusion may be rapid on the wall of a wider capillary. At the low pressures where molecular streaming occurs the isotherm will obey Henry's law and

$$\frac{\text{concentration on surface}}{\text{concentration in gas phase}} = \frac{C_s}{C_1} = k_3$$

The flow in the x-direction in the gas phase is given by

$$\frac{\partial n_1}{\partial t} = -\pi r^2 D \frac{\partial c_1}{\partial x}$$

where D is given by eqn. (33). The flow on the surface is similarly

$$\frac{\partial n_s}{\partial t} = -2\pi r \, D_s \, \frac{\partial c_s}{\partial x}$$

and thus the total flow at the point x is

$$\frac{\partial n_1}{\partial t} + \frac{\partial n_s}{\partial t} = -\pi r^2 \left\{ D + \frac{2D_s \, k_3}{r} \right\} \frac{\partial c_1}{\partial x} = -\pi r^2 D' \frac{\partial c_1}{\partial x} \quad . \quad (34)$$

In the periodic potential field due to the surface forces $D_s = D_0 \, e^{-E/RT}$ and so from the time lag L one measures

$$D' = \frac{4r^2}{3r \, . \sqrt{\frac{\pi m}{2kT}} + \tau} + \frac{2D_0}{r} \, . \, k_3 \, . \, e^{-E/RT} \quad . \quad . \quad (35)$$

A further substitution for k_3 is possible on equating rates of evaporation and condensation of molecules: $k_3 = \sqrt{\frac{kT}{2\pi m}}$

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[26] Barrer, *Trans. Faraday Soc.*, 1944, **40**, 555.

[27] Barrer and Ibbitson, *Trans. Faraday Soc.*, 1944, **40**, 206.

Experimental data in this interesting region where the channels are very narrow indeed ($r \sim 10^{-6}$ to 10^{-7} cm.) are confined to observations by Rayleigh[28] who pressed optically plane glass plates together and allowed gases to permeate between them. He observed, as eqn. (35) implies, that Knudsen's equation was no longer applicable. Eventually as the channel becomes still narrower the diffusing species never leave the field of the surface forces, and " surface " diffusion alone is present. Results obeying the equation $D_s = D_0 e^{-E/RT}$ have been obtained when gases flow through silica glass[29] or into dehydrated zeolite crystals.[25 26 27]

Summary

A fluid such as water may need to be treated as incompressible, compressible but still condensed, or gaseous, according to conditions of temperature and pressure. Steady and transient states of flow of fluids in these conditions have been briefly considered. The displacement of one fluid by another has been examined and the relative roles played by pressure-head and surface tension. Molecular mechanisms of gas or vapour flow in single capillaries and in porous media, and transition regions from one flow mechanism to another have been particularly considered, from high-pressure flow in wide tubes until the pore radius is so small that the diffusing species move entirely within the range of surface forces.

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[28] Rayleigh, *Proc. Roy. Soc. A*, 1936, **156**, 350.

[29] Cp. ref. [4], Ch. 3, where a summary of data on flow in zeolites and in silica glass is given up to 1940.

SOME PHYSICAL ASPECTS OF WATER FLOW IN POROUS MEDIA

By P. C. Carman

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The permeability of a medium to water or any other fluid under the action of a pressure difference may arise in various ways.

(i) The fluid may dissolve and be transported by diffusion along a concentration gradient produced by the pressure difference.

(ii) In a porous medium, the fluid may be adsorbed at the internal walls of the capillary structure and be transported by diffusion along a concentration gradient.

(iii) The fluid may flow through capillaries of a porous medium at a rate limited merely by its viscosity.

No sharp line separates these processes and it is possible for all to be involved simultaneously. Whether water flows through a cellulose membrane in ultrafiltration by processes (i), (ii) or (iii), or by more than one simultaneously is an unsettled question, and a very important one. If a gas flows through capillaries narrower than the mean-free-path of the gaseous molecules, viscous flow gradually gives way to diffusion or " molecular flow."

While processes (i) and (ii) are of particularly vital interest to chemists, they belong essentially to the study of diffusion and will be discussed by others. The present paper is concerned merely with viscous flow, since an understanding of this must form the background to more complex problems. Further, though it is relatively simple, the danger of over-simplification has not always been properly realised.

Pore Diameters by Permeability

Permeabilities are widely used to assess, say, the pore size of a sintered-glass plate, assuming that viscous flow alone takes place. Now, the rate of viscous flow in a circular capillary of diameter d_e cm. is given by Poiseuille's law,

$$u_e = \frac{d_e^2 \Delta P}{32\ \eta\ L_e} \quad . \quad . \quad . \quad . \quad (1)$$

where u_e = rate in cm./sec., ΔP = pressure difference in dynes/cm.^{2} along a length L_e, η = viscosity of fluid in poises. Suppose that Q cm.^{3}/sec. flow through a porous plate of area A cm.^{2} and thickness L cm. under the same pressure difference. The apparent velocity $u = \frac{Q}{A}$ whence, if we assume the plate is equivalent to a bundle of circular capillaries with diameter equal to the pore size d_1, then the latter is given by

$$d_1 = \sqrt{\frac{32\ u\eta L}{\Delta P}} \quad . \quad . \quad . \quad . \quad (2)$$

A porous medium, however, is most decidedly not equivalent to a bundle of circular capillaries. Its capillaries are non-circular, tortuous and connect into one another, so that the pore size given by (2) cannot be a reliable measure of the actual size of capillary spaces. Some average pore size must be chosen and, if it is measured by permeability, it cannot have any physical meaning unless it is a quantity which characterises viscous flow.

Now, when strict mathematical equations are worked out for viscous flow in non-circular capillaries of known shape, it is found empirically that they can be put in the form.

$$u_e = \frac{m^2}{k_0 \eta} \cdot \frac{\Delta P}{L_e} \quad . \quad . \quad . \quad . \quad (3)$$

where m is the "hydraulic radius,"[1] i.e., the ratio of area of cross-section to perimeter of cross-section, or volume of capillary to surface of capillary. For a circular capillary, $d_e = 4m$ whence, from eqn. (1), $k_0 = 2$. For flow between two parallel plates, $k_0 = 3$, and for most other shapes, k_0 varies only between 2·0 and 2·5, indicating that the most significant "average diameter" for a non-circular capillary with respect to viscous flow is $4m$.

In a porous medium of thickness L, the fractional free area of a cross-section is equal to the porosity ε, and the actual length of a capillary is L_e, whence the actual velocity u_e is given by

$$u_e = \frac{u}{\varepsilon} \cdot \frac{L_e}{L} \quad . \quad . \quad . \quad . \quad (4)$$

Substituting in (3)

$$u = \left(\frac{L}{L_e}\right)^2 \cdot \frac{m^2 \varepsilon}{k_0} \cdot \frac{\Delta P}{\eta L} \quad . \quad . \quad . \quad . \quad (5)$$

As neither $\frac{L_e}{L}$ or k_0 can be evaluated separately, they can be combined to give

$$k = k_0 \left(\frac{L_e}{L}\right)^2 \quad . \quad . \quad . \quad . \quad . \quad (6)$$

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[1] Carman, *Trans. Inst. Chem. Eng.*, 1937, 15, 150.

Eqn. (5) can be checked by using unconsolidated beds of particles of known shape, and hence of known specific surface S_0 $\text{cm.}^2/\text{cm.}^3$, since m can then be calculated,

$$m = \frac{\text{pore volume}}{\text{surface area of particles}} = \frac{\varepsilon}{(1-\varepsilon)S_0} \quad . \quad . \quad (7)$$

Experiments over a wide range of conditions[2,3] have confirmed eqn. (5) with reasonable accuracy if k is given the value 5·0, i.e.,

$$u = \frac{m^2\varepsilon}{5\eta} \cdot \frac{\Delta P}{L} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

This is generally known as the Kozeny law.[4] It is admittedly semi-empirical, being derived by analogy, but it is successful, and it can therefore be firmly stated that

$$d_2 = 4m = \sqrt{\frac{80\, u\eta L}{\varepsilon\, .\, \Delta P}} \quad . \quad . \quad . \quad . \quad (9)$$

is the only "pore diameter" calculated from permeability data which has any physical meaning. It may be noted that, if $\varepsilon = 0{\cdot}4$, d_2 is $2{\cdot}5 \times d_1$.

Limitations of Kozeny's Law.—Though eqn. (8) can only be tested experimentally for unconsolidated beds, it should also be true for consolidated media. In any case, if it is not, there is no alternative, and permeability must then be regarded as unreliable for measurement of pore size. Conditions for its validity are therefore important. They may be summarised as follows.

(i) No pores are sealed off.
(ii) Pores are distributed at random.
(iii) Pores are reasonably uniform in size.
(iv) Porosity is not too high.
(v) Diffusion and surface effects are absent.

Condition (i) is obvious, since sealed pores give an "effective porosity" for flow which is less than the total porosity. This is quite common in well-fired ceramic materials, but the effective porosity can often be measured, e.g., by water-absorption tests on building bricks.

Condition (ii) may not apply in stratified materials, e.g., certain sandstones show a greater permeability parallel to the bedding plane than across it.[5] An extreme case of oriented distribution of pores was studied by Sullivan and Hertel,[6] namely, fibres packed parallel to one another. They found that, perpendicular to the fibres, the constant k in eqn. (8) increased to 6·0, and that, parallel to them, it decreased to 3·0, though, otherwise, the equation is obeyed.

Condition (iii) is one which is most difficult to fulfil, and is perhaps only experienced in beds of uniform, spherical particles, or in sintered plates made from closely sized particles of glass or of metals. Causes of error in this respect are several and will be taken in turn.

(*a*) Non-uniformity of particle size in an unconsolidated or in a sintered plate does not necessarily mean non-uniform pores, particularly if *proportions* are distributed evenly over the range of sizes. A small proportion of large particles in a large proportion of small ones can give uniform pores, but the converse is almost certain to give a mixture of small and large pores. This is equivalent to large and small capillaries in parallel, a condition

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[2] Carman, *J. Soc. Chem. Ind.*, 1938, **57**, 225; *J. Soc. Chem. Ind.*, 1939, **58**, 1.
[3] Wiggins, Campbell and Maass, *Can. J. Res. B*, 1939, **17**, 318.
[4] Kozeny, *Ber. Wien Akad.*, 1927, **136a**, 271.
[5] Muskat and Botset, *Physics*, 1931, **1**, 27.
[6] Sullivan and Hertel, *J. Appl. Physics*, 1940, **11**, 761.

giving a higher permeability than if the same porosity is distributed uniformly.[7] In other words, the pore size obtained is nearer to the size of the largest pores than to the true average. In a consolidated porous medium, any small cracks, blow-holes, etc., will lead to unduly high permeabilities.

(*b*) A very wide range of pore sizes in an unconsolidated bed makes it difficult to avoid *segregation* into layers of different size distribution. Even if porosity is uniform throughout the bed, the permeability will be lower than should be expected, i.e., undue weight is given to the smallest pores. Segregation is really an example of non-random distribution and, in a consolidated medium, would give high permeability in a direction parallel to the stratification. It may be noted that non-uniform particle sizes can give non-uniform pores, increasing permeability, and segregation, decreasing permeability.

(*c*) Small particles tend to form aggregates with relatively large spaces between them, thus giving too high a permeability. This is a surface effect and rapidly becomes more marked for particles below 10μ in size. A liquid which wets particles and promotes dispersion tends to prevent aggregation. Thus, Portland cement obeys Kozeny's law with alcohol, which disperses it, but not with *n*-hexane, which causes it to flocculate. Compression tends to reduce large voids first, giving greater uniformity, so that, if a bed of cement in *n*-hexane is first compressed strongly by a piston, the permeability conforms to Kozeny's law.[8] Needle-shaped, fibrous and flat-sided particles tend to form aggregates with large voids between them, due to their shape, and only obey Kozeny's law if great care is taken to ensure uniformity of packing.

Condition (iv) results from the fact that eqn. (8) is based upon an analogy. The strict equation for flow parallel to equi-spaced circular cylinders was worked out by Emersleben,[9] and this shows that the Kozeny analogy should break down seriously when $\varepsilon > 0{\cdot}8$. A study of flow parallel to a bundle of fibres was made by Sullivan,[10] who showed that k ceased to be constant, but increased rapidly with ε at high porosities, in accord with Emersleben's predictions. The error was, in general, not serious till $\varepsilon > 0{\cdot}9$, possibly because fibres were not equi-spaced and imperfectly aligned. This limitation of eqn. (8) is only liable to be experienced for fibres.

Condition (v) brings in a host of unsolved problems, especially for flow of water and other liquids, but these are really outside the scope of this paper, and can only be mentioned. One of the most important is flow of water through clays. If substitution for m is made in eqn. (8), a porosity function $\frac{\varepsilon^3}{(1-\varepsilon)^2}$ is obtained which varies extremely rapidly with ε. Despite this, the water permeability of most clays changes very much more rapidly with ε, and a suggestion of Kozeny[11] that part of the pore water remained stationary was followed up by the writer.[12] It was further suggested that this might be water of swelling for montmorillonite clay minerals, but doubt is felt about this, particularly in view of enormous changes in permeability with porosity found by Macey.[13] The empirical equation used by Macey has no physical basis. Obviously, the water permeability of clays is a vital part of the whole important question of clay-water relationship.

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[7] Ref. [1], p. 156.
[8] Rigden, *J. Soc. Chem. Ind.*, 1947, **66**, 130.
[9] Emersleben, *Z. Physik*, 1925, **26**, 601.
[10] Sullivan, *J. Appl. Physics*, 1941, **12**, 503.
[11] Kozeny, *Kulturtechniker*, 1932, **35**, 478.
[12] Carman, *J. Agric. Sci.*, 1939, **29**, 262.
[13] Macey, *Proc. Physic. Soc.*, 1940, **52**, 625.

Changes of viscosity in narrow capillaries have been suggested, but seem unlikely.[14]

Permeabilities should be inversely proportional to viscosity, but, in certain cases, this is not true.[15] Again, a satisfactory explanation has not been found for a steady decrease of permeability with time found sometimes for flow of water and aqueous solutions through porous plates.[16] In brief, permeabilities of liquids in very fine-pored media are very liable to be controlled by surface effects, particularly in the case of water.

In contrast to liquids and to easily condensed vapours, the flow of permanent gases in fine-pored media is now well understood.[8, 17] The main departures from eqn. (8) are due to " slip-flow " and " molecular flow," and so successful are the modified equations that air permeabilities have been used by Arnell[18] to measure the surface of particles as fine as carbon blacks, giving results in excellent agreement with electron microscope and nitrogen adsorption measurements.

Surface and Size Measurements.—The application of eqn. (8) to measure specific surface of particles and of porous media in general is obtained by substituting $m = \frac{\varepsilon}{(1 - \varepsilon)S_0} = \frac{\varepsilon}{(1-\varepsilon)\rho_1 S_1}$ where ρ_1 = density of solid in g./cm.^{3} and S_1 is specific surface in cm.^{2}/g. The method has now been so widely developed and applied[2, 3, 19, 20] that only one special aspect will be considered here. As an example, the simplest method of finding the diameter of cellulose fibres dispersed in water as in a paper pulp is to form them into a bed and measure the water permeability.[21] The diameter follows from the specific surface. Unfortunately, though the weight of cellulose per unit volume of bed, W g./cm.^{3}, can be measured, the fibres are swollen to an extent which is very difficult to ascertain, so that, in effect, the density ρ_1 is unknown, and ε cannot be calculated. Now $(1 - \varepsilon) = \frac{W}{\rho_1}$ whence

$$m = \frac{\left(1 - \frac{W}{\rho_1}\right)}{WS_1}$$

and, from (8)

$$u = \frac{\left(1 - \frac{W}{\rho_1}\right)^3}{5W^2{S_1}^2} \cdot \frac{\Delta P}{\eta L} \quad . \quad . \quad . \quad . \quad . \qquad (8a)$$

In this, both ρ_1 and S_1 are unknown, but, in a bed of fibres, the porosity, and hence W, can be varied over a wide range by compression, so that, if one plots $\left(\frac{5W^2 u\eta L}{\Delta P}\right)^{1/3}$ against W, a straight line should be obtained. The intercept for $W = 0$ equals $\frac{1}{S_1^{2/3}}$ whence S_1 is obtained. Further, the gradient is $-\frac{1}{\rho_1 S_1^{2/3}}$, so that ρ_1 is also obtained. In this way, additional valuable information is gained, e.g., ρ_1 decreases when a pulp is beaten, indicating that cellulose fibres have become more hydrated. The same method of analysis has been applied to air permeabilities of cotton and wool fibres.[22]

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[14] Bastow and Bowden, *Proc. Roy. Soc.* A, 1935, **151**, 220.

[15] Bozza and Secchi, *Giorn. Chim. Ind.*, 1929, **11**, 443 and 487; Bull and Wronsky, *J. Physic. Chem.* 1937, **41**, 463.

[16] Buche, *V.D.I. Beit. Verfahrenstechnik*, 1937, **5**, 155; Mehner, *Chem. Fabr.*, 1937, **10**, 2.

[17] Arnell, *Can. J. Res. A*, 1946, **24**, 103; Carman, *Nature*, 1947, **160**, 301.

[18] Arnell, *Can. J. Res.*, *A*, 1948, **26**, 29.

[19] Sullivan and Hertel, *Advances in Colloid Science* Vol. 1 (1942). Edited by Kraemer, Bartell and Kistler, ch. 2, p. 37.

[20] Lea and Nurse, *Symposium on Particle Size Analysis* (Institution of Chem. Eng. and Soc. Chem. Ind.), Feb., 1947.

[21] Mason, Pulp and Paper Research Institute, Montreal, Canada (private communication).

Pore Diameters by Capillarity Measurements.—The height of capillary rise of water in a porous medium, generally measured by the maximum bubble pressure method, is used much more often than permeabilities for calculating pore diameters. In a circular capillary, the diameter would be given by

$$d_e = \frac{4\sigma}{\rho g h}$$

where σ = surface tension in dynes/cm. and h = height of capillary rise in cm., and this equation is used also for pore diameters. The calculation is sound, since, in non-circular capillaries and in porous media, $4m$ takes the place of d_e.[23]

Thus,
$$d_2 = 4m = \frac{4\sigma}{\rho g h}$$

Since $m = \frac{\varepsilon}{(1-\varepsilon)S_0}$ this can be checked with particles of known shape, and been found to be reasonably correct[24]; but the method itself is very open to uncertainty, due to what may be called "meniscus errors." In a circular capillary, the meniscus is easily allowed for. In a non-circular one, the meniscus does not rise evenly all round the perimeter, particularly if the latter possesses sharp angles. This is greatly exaggerated in a porous medium and, in fact, the ability of water to move into a porous structure without filling the pores is a phenomenon of outstanding importance.[25] The measurement of the "capillary rise," i.e., the height to which water will fill the pores, thus becomes very uncertain.

It must also be noted that measurement by the bubble pressure method is even more sensitive than permeability to non-uniformity of pore size. In fact, the measurement is best referred to the pressure required to produce an arbitrary rate of bubbling than to the first appearance of bubbles, to prevent the largest pores carrying too great a weight.

Summary

When flow in a porous medium is controlled by viscosity only, it obeys the Kozeny-Carman law with remarkable accuracy, and it is pointed out that the only rational pore diameter calculable from permeability measurements is $d_2 = 4 \times$ (hydraulic radius) (m). Certain conditions must be fulfilled for permeability measurements to have significance for calculation of pore diameters or specific surface, and these are discussed in some detail.

As the permeability method for specific surface is well established, attention is merely directed to its extension to give both density and diameter of cellulose fibres in paper pulps. Pore diameters as normally calculated by the bubble pressure method are equal to $4 \times$ (hydraulic radius) and should therefore equal d_2 calculated from permeability. The method, however, is open to considerable uncertainty and error.

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[22] Cassie, *J. Text. Inst.*, 1942, **33**, 195.
[23] Ref. [1], p. 154.
[24] Carman, *Soil Sci.*, 1941, **52**, 1.
[25] Schofield, *Trans. 3rd Int. Congr. Soil Sci.*, 1935, **2**, 38.

SOIL GEOMETRY AND SOIL-WATER EQUILIBRIA

By E. C. Childs and N. C. George

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Physically a soil may be regarded as completely specified by the geometry of the interface between the solid component and the void space together with that of the air-water interface within the voids. In the nature of the case it is most unlikely that a complete geometrical specification will ever be accomplished and one must be satisfied with less. The determination of the size distribution of the ultimate particles (mechanical analysis) and of aggregates stable to arbitrary degrees of violence, which constitute factors of the soil geometry, have long been weapons in the armoury of the soil scientist, but from this information alone one can only infer qualitatively the nature of the void space. In recent years the direct determination of pore-size distribution has become increasingly recognised as a complement to mechanical analysis[1] [2] [3] [4] [5] [6] [7]; and on its behalf it may be said that it is the water-occupied void space which, together with the solid surface, is the seat of physico-chemical activity and which largely determines the gross physical properties of the soil. The complete geometrical specification which the soil scientist seeks under the name " soil structure " may indeed be a will-o'-the-wisp, but it is reasonable to suppose, and we seek to show, that certain measurable physical properties of the soil may be related to measurable factors in soil geometry.

It is not our present function to discuss the physical chemistry of the soil solution, but some qualitative description must be included in the discussion of the determination of pore-size distribution. The total force acting on a volume element of water in the void space may be regarded as made up of four components, each making a greater or less contribution according to such circumstances as the nature of the solid surfaces, the moisture content, the content of soluble salts and the location of the element considered. The four components are: (*a*) gravitational attraction, always acting vertically downward, (*b*) hydrostatic pressure difference, (*c*) osmotic pressure differences due to differences of content both of soluble salts and of anions and cations in Gouy double-layers associated with the solid surfaces, and (*d*) adhesion of water to the solid surfaces. It simplifies matters if we speak in terms of the scalar potential rather than the vector force, defining the potential difference between points A and B as the work done against the above-described force field in translating unit volume of water from the point A to the point B, and, as usual, adopting the potential at one convenient point as our arbitrary zero potential. The potential at any point will then be the scalar sum of four components corresponding to the four groups (*a*) to (*d*). The water is in hydrostatic equilibrium when the total force is everywhere zero, that is, when the total potential is everywhere the same, notwithstanding that single components may vary widely from point to point.

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[1] Childs, *Soil Sci.*, 1940, **50**, 239.

[2] Childs, *Soil Sci.*, 1942, **53**, 79.

[3] Donat, *Trans. 6th Comm. Int. Soc. Soil Sci. B*, 1937, p. 423.

[4] Haines, *J. Agric. Sci.*, 1930, **20**, 97.

[5] Leamer and Lutz, *Soil Sci.*, 1940, **49**, 347.

[6] Schofield, *Trans. 1st Comm. Int. Soc. Soil Sci. A*, 1938, p. 38.

[7] Swanson and Peterson, *Soil Sci.*, 1942, **53**, 173.

The gravity component needs no explanation. The work done in lifting unit volume of water (density ρ) to a height h above an arbitrary datum level, and therefore the potential at height h, is given by $g\rho h$. The hydrostatic pressure term (*b*) is also familiar. If S is the surface tension, and the air-water interface in which it acts has radii of curvature r_1 and r_2, then the pressure on the water side of the surface is less than that in the air by the amount $\Delta P = S(1/r_1 + 1/r_2)$, where r_1 and r_2 are regarded as positive for curvatures which are concave to the air. It is convenient to take atmospheric pressure as our datum; then the pressure P just inside an interface between soil water and air which is continuous with the outside air is given by $P = -S(1/r_1 + 1/r_2)$. P may, of course, take other values at points remote from the interface. It is common to ignore the negative sign and to speak of pressure deficiency or suction pressure. The work done in taking unit volume of water from a point of zero pressure to one of pressure P, and consequently the potential at the latter point, is given by P. The osmotic pressure term is less well defined. According to Gouy's well-known concept,[8] a surface dissociating, say, cations, itself having a negative charge, tends to maintain increased cation and decreased anion concentration in its vicinity as compared with the equal concentrations in the more remote solution. From this it is a simple consequence of the Donnan equilibrium that the total ion concentration, and therefore the osmotic pressure, increases as the solid-liquid interface is approached; the equilibrium of the double-layer is a balance of the concentrating electric and adsorbtive forces as opposed to the diluting osmotic pressure. Corresponding to this equilibrium there is an osmotic pressure gradient which is a function of distance from the solid surface. The osmotic pressure p at any point corresponds to a hydraulic potential contribution $-p$, since it must be regarded as a hydrostatic pressure deficiency. This contribution to potential might commonly be appreciable for distances up to the order of 50 A. from the dissociating surface, but there seems to be no experimental confirmation of this osmotic potential distribution. Even less is known about the adhesion potential due to the attraction between the solid surface and the water dipolar molecules, but from the nature of dipole attraction these adhesion forces, whilst they may attain large values at close distances of approach, must be of very short range. Since the force is an attraction, the potential contribution will be negative relative to a point in the more remote solution; let us call it $-\pi$ where π is positive.

The total potential, φ, is the sum

$$\varphi = g\rho h + (P - p - \pi) \quad . \quad . \quad . \quad (1)$$

The total potential being everywhere the same at equilibrium, the hydrostatic pressure at a given height will vary as p and π vary, in such a way as to keep the term in brackets constant. In particular, there is no reason why P should not assume positive values in the immediate vicinity of solid surfaces where p and π may become large.

The total potential may be measured by allowing the soil system to come into equilibrium with a system of known potential components. Such a system may commonly be a manometer, the only potential components being directly measurable gravitational potential and hydrostatic pressure; equilibrium may be attained either by adjusting the manometer column [4] or by altering the soil air-pressure, thus changing the arbitrary pressure datum, as in the pressure-plate method of Richards.[9] Alternatively the soil system may be brought into equilibrium, via the vapour phase, with a hypothetical water surface at a hydrostatic pressure calculable from the vapour pressure. Potential measurements by means of freezing point depression seem to be ambiguous of interpretation, since the results depend upon whether one assumes the ice formed to be released or not released from the pressure deficiency,[10] [11] but fortunately the potential range for which this method is particularly suited is readily covered by the pressure-plate method. The total potential being known, the sum $(P - p - \pi)$, which we may call ψ, is clearly known, but we cannot at present precisely assess the separate contributions. We may write (1) in the form, $\varphi = g\rho h + \psi$, and ψ is referred to as the capillary potential, without intentional stressing of the surface tension component which the term connotes. The capillary potential is commonly expressed as a pressure deficiency, from its method of measurement, and is not to be understood as referring necessarily to the hydrostatic pressure within the soil solution.

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[8] Gouy, *J. Physique*, 1910, (4) 9, 457.

[9] Richards and Fireman, *Soil Sci.*, 1943, 56, 395.

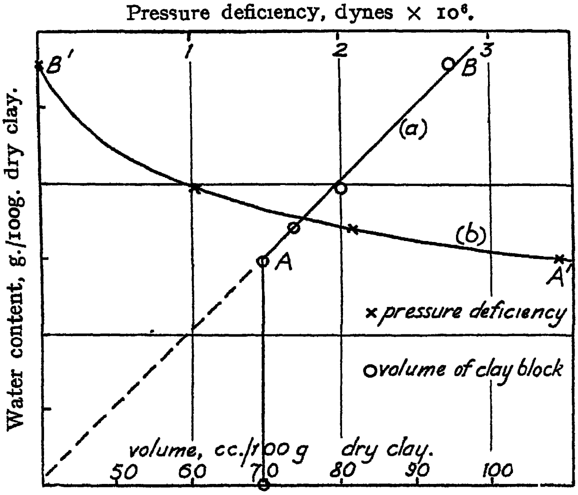

FIG. 1.—Moisture characteristic and shrinkage curve for a kaolin clay block.

The capillary potential components, and therefore ψ itself, will determine the moisture content of a given soil. The void space is continuous but not of uniform cross-section. It may be regarded as a series of cells connected to others via channels of smaller cross-section. For a given pressure deficiency a cell will be empty of water if its largest interconnecting channel is too large to accommodate an air-water interface of sufficiently sharp curvature to maintain that pressure deficiency.[4] As the suction is increased, cells will empty in succession, giving a suction–moisture-content curve characteristic of the soil; such curves have been called moisture characteristics.[1] If we make the assumption that large interconnecting channels are associated with large cells, and if we are justified in ignoring the contributions of p and π to ψ (as in the case of non-shrinking, light, sandy soils at all but the lowest moisture contents), the moisture characteristic may clearly be interpreted as indicating the pore-size distribution in the soil. The moisture characteristic of a structured clay soil at low pressure deficiency can also be interpreted as the size distribution of the inter-crumb pores,[1] which are large enough for the contributions of p and π to be negligible in this range of ψ.

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[10] Edlefsen and Anderson, *Hilgardia*, 1943, 15, 31.

[11] Schofield and Botelho da Costa, *J. Agric. Sci.*, 1938, 28, 644.

By contrast, Fig. 1 *a* and 1 *b* shows the moisture characteristic and the shrinkage curve (following Haines) respectively of a kaolin clay block initially wetted beyond the "sticky point." The range AB of Fig. 1 *a* corresponds to the range A′B′ of 1 *b*, and it will be seen that practically the whole loss of water is accounted for by a decrease of total volume, the initial and final air contents differing by only 1 cc./100 g. dry clay. The mechanism of water removal is clearly not that which enables us to interpret the moisture characteristic as a reflection of pore-size distribution. The suction removes water by drawing the solid particles closer together, whether by orientation of the kaolin mineral plates into lower potential energy positions or by interpenetration of double-layers.[12]

The pressure required to allow water to re-enter an empty cell is higher (the suction less) than that at which the cell emptied, and consequently a moisture characteristic of the first-mentioned type is not reversible but shows hysteresis.[4] The difference between the emptying- and filling-pressure will depend upon the relative sizes of the cell and connecting channels, and most characteristics cannot be explained without assuming a proportion of cells which show little or no hysteresis.

If moisture characteristics of the second type involve a reorientation of mineral particles, they also might be expected to be irreversible, for one cycle at least of moisture change, so that the presence of hysteresis is not necessarily an indication of a particular mechanism of drying, nor a sure guide to the interpretation of the characteristic. Re-wetting of the kaolin sample already referred to could not readily be carried out in our pressure-plate apparatus, but an almost uncontrolled re-wetting to the "sloppy point" brought the moisture content and volume back to the initial values; we cannot therefore say there was no hysteresis shown by this sample, but there was no non-recoverable shrinkage. We propose in the near future to compare results of this kind with moisture and volume changes of the same materials under direct applied pressure.

Perhaps the soil property most obviously governed by pore-size distribution is the permeability to fluids. Formulæ have been proposed independently by various workers,[13] [14] [15] relating permeability to porosity and specific surface, and bearing a close resemblance to one another. In general it may be said that too small a range of experimentally available porosity prevents a satisfactory test as regards this factor, but, as regards specific surface, there is fair agreement between experiment and theory for such materials as have independently calculable specific surface. Such theories may be criticised on the grounds that, whilst porosity and specific surface are uniquely determined by the void-space geometry, which also determines permeability, the converse is not true, and it is possible to conceive of different pore-size distributions, with presumably different permeabilities, yet having the same porosity and specific surface. Further, the void-space geometry undoubtedly accounts for the anisotropy which most soils exhibit to greater or less degree, since, for example, a structured soil with cracks lying predominantly in equipotential planes has lower permeability than that same soil with the equipotential planes perpendicular to the cracks. The specific surface would, of course, be the same in both cases, and might, moreover, be very little affected by the presence of the cracks, to which appreciable permeability is primarily due. Empirical approaches to the relationship between pore-size distribution and permeability have been made by attaching varying weight to the contributions of pores lying in various size-groups.[16] [17] [18]

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[12] Schofield, *Trans. 3rd Int. Congr. Soil Sci.*, 1935, **1**, 30.

[13] Fair and Hatch, *J. Amer. Waterworks Assoc.*, 1933, **25**, 1551.

[14] Kozeny, *Ber. Wien Akad.*, 1927, **136a**, 271.

[15] Zunker, *Trans. 6th Comm. Int. Soc. Soil Sci.* B, 1933, p.18.

We have sought a theoretical treatment which brings out more clearly than hitherto the mechanism involved, and have tested it by measurements on a coarse sand fraction in which the pore-size distribution is certainly to be inferred from the moisture characteristic. The test permits the study of a great range of effective porosities, and also results in a measurement of direct interest in soil science, namely, the variation of soil permeability with moisture content.

Consider two soil columns of unit cross-section; the exposed ends, A and B, will exhibit pore-size distributions $f(r)$ and $F(r)$ where $f(r)\delta r$ is the area of A devoted to pores of size between r and $r + \delta r$, whilst $F(r)$ is similarly defined with respect to B. $F(r)$ and $f(r)$ are revealed by the moisture characteristic alone if the sand is isotropic, but may need the assistance of direct microscopic examination in various planes if the medium is anisotropic. When A and B are brought together to constitute a continuous column, the total area devoted to the sequence of a pore of size σ followed or preceded by one of size ρ will be proportional to $f(\sigma)\delta r \,.\, F(\rho)\delta r + f(\rho)\delta r \,.\, F(\sigma)\delta r$. If both columns consist of similar soil, so that the whole is a uniform-conducting column, then $f(r)$ is identical with $F(r)$, and the area devoted to the given sequence is proportional to $f(\sigma)\delta r \,.\, f(\rho)\delta r$. We shall make two assumptions which involve small errors in opposite senses; first, that cells make no contribution to permeability other than by the *direct* sequence of the above type, and second that the permeability contribution is limited by the smaller cell in the sequence. The first assumption, by ignoring leakage via more devious paths, underestimates permeability, the second, by ignoring the potential-drop in the larger cell, overestimates it. Suppose $\sigma < \rho$; then the number of flow-limiting cells in the sequence cross-section considered is proportional to $f(\sigma)\delta r \,.\, f(\rho)\delta r/\sigma^2$. By Poiseuille's equation, the contribution to flow of each individual cell-sequence is proportional to σ^4, hence the contribution, δK, of all the cells of this sequence to the permeability is $\delta K \propto f(\sigma)\delta r \,.\, f(\rho)\delta r \,.\, \sigma^2$ and the total permeability, K, is given by

$$K \propto \sum_{\sigma=0}^{R} \sum_{\rho=0}^{R} f(\sigma)\delta r \,.\, f(\rho)\delta r \,.\, \sigma^2 \qquad . \quad . \quad . \qquad (2)$$

In (2) the final factor changes to ρ^2 when $\rho < \sigma$. The summation is carried out numerically from the moisture characteristic, and by stopping at a chosen value R one can compute the permeability of a soil at any desired moisture content, i.e., at a desired effective porosity.

The experimental determination of permeability at varying moisture content is beset with difficulties. The hydraulic potential gradient which produces the flow also plays its part in determining the moisture content, which therefore varies along the flow-path. Determinations both of the potential gradient and of moisture content are not straightforward. However, if one can employ a sufficiently long column, it has been shown[19] that the moisture content and pressure deficiency are sensibly constant over a considerable length. The potential gradient in a vertical column is therefore the gravitational gradient only and is known without measurement. Constancy of moisture content enables one to use indirect electrical (apparent capacitance) methods of measurement of moisture content without the use of troublesome guard-rings in alternating current circuits. Manometers

[16] Baver, *Proc. Amer. Soil Sci. Soc.*, 1938, **3**, 52.
[17] Nelson and Baver, *Proc. Amer. Soil Sci. Soc.*, 1940, **5**, 69.
[18] Smith, Browning and Pohlson, *Soil Sci.*, 1944, **57**, 197.
[19] Childs *Soil Sci.*, 1945, **59**, 405.

were used only to indicate when conditions were steady after a change of rate of flow.

Fig. 3 shows the computed permeability curve for a sand fraction (moisture characteristic as in Fig. 2) separated between the 1 mm. and 0·5 mm. sieves, together with the experimentally observed curve, with which the computed curve was matched at an arbitrary point. A second set of points was obtained for the condition of increasing moisture content, which was occasionally accidentally achieved by a momentary blockage of the inlet syphon feeding the flow-tube followed by a resumption of full flow. We have not

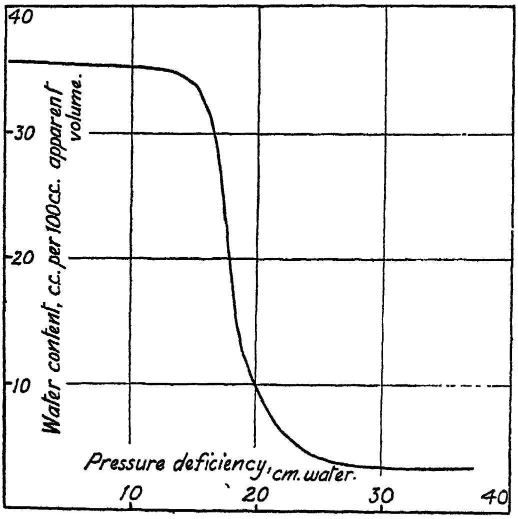

FIG. 2.—Moisture characteristic of a sand fraction used in obtaining subsequent figures.

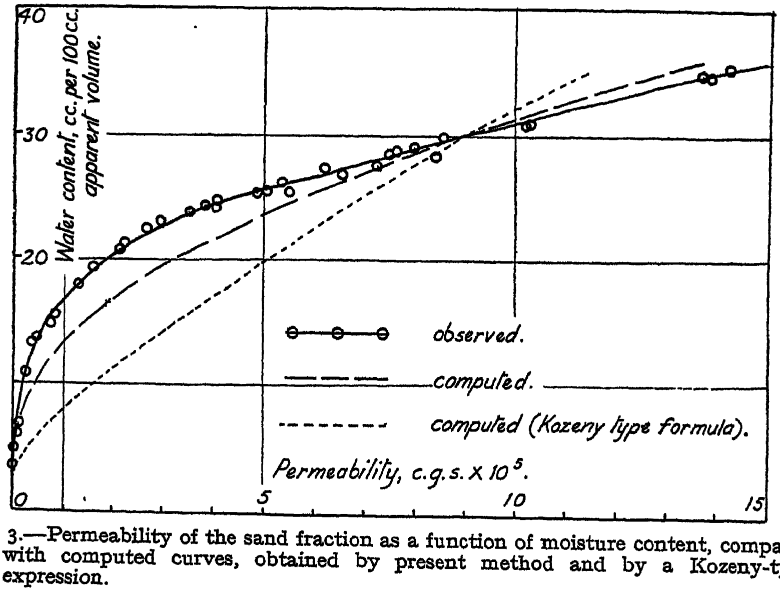

FIG. 3.—Permeability of the sand fraction as a function of moisture content, compared with computed curves, obtained by present method and by a Kozeny-type expression.

reproduced this curve since we have not yet enough points, but it seems that the permeability *at a given moisture content* is greater when that content is decreasing than when it is increasing, which argues a different distribution of water. A curve computed from a Kozeny-type formula, matched at the same point, is also given.

The dependence of permeability upon moisture content has long been recognised in the definition of the so-called "lento-capillary point," the moisture content of soil at which the permeability is no longer appreciable. The "definition" is, of course, vague and no more than a qualitative appreciation of an observed phenomenon, and we can see that there really is no such recognisable point. Another "moisture constant" illuminated by this discussion is the "field capacity," usually untenably defined as the moisture content of soil when freely draining under gravity. The field capacity is a property which is obtrusive mainly in dry regions where irrigation is practised. The observed facts are that water moves down the soil profile relatively rapidly during the irrigation and for a few days subsequently, the added water redistributing itself to wet a certain depth to a certain moisture content. Thereafter the water moves relatively slowly, moisture content changes being due mainly to removal by the crop. There is no suggestion of complete attainment of equilibrium, but only of a sudden rapid decrease of movement after an initial free-moving stage. The moisture content at the assessed "end" of this initial stage is the field capacity. Redistributions of water of this kind are reminiscent of diffusion.[20] Darcy's law, for a vertical potential gradient, is

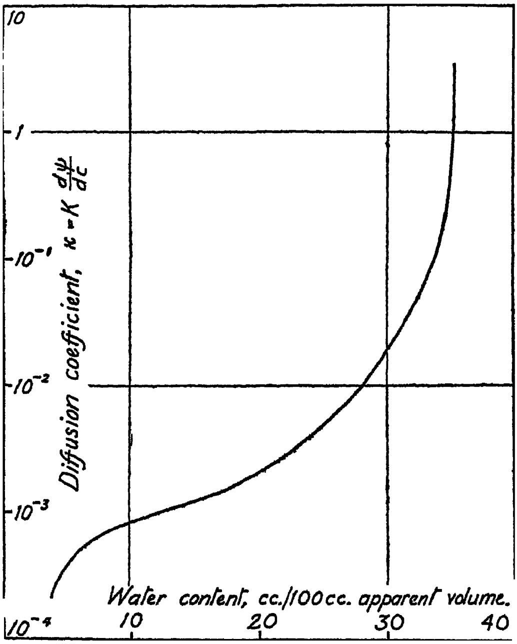

FIG. 4.—Diffusion coefficient of the sand fraction as a function of moisture content.

$$dq/dt = -K\,d\varphi/dh \quad . \quad . \quad . \quad . \quad (3)$$

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[20] Childs, J. Agric. Sci. 1936, 26, 527.

or

$$\mathrm{d}q/\mathrm{d}t = -K\,\{g\rho + (\mathrm{d}\psi/\mathrm{d}c)\,(\mathrm{d}c/\mathrm{d}h)\}\;. \quad . \quad . \quad . \qquad (4)$$

where $\mathrm{d}q/\mathrm{d}t$ is the apparent flow velocity, h is height above datum and c is the moisture content. Eqn. (4) is the diffusion equation with diffusion coefficient κ given by

$$\kappa = K(g\rho\,.\,\mathrm{d}h/\mathrm{d}c + \mathrm{d}\psi/\mathrm{d}c)\,. \quad . \quad . \quad . \quad . \qquad (5)$$

The term $g\rho\,.\,\mathrm{d}h/\mathrm{d}c$ will often be negligible. Fig. 4 shows $K\mathrm{d}\psi/\mathrm{d}c$ as a function of c, for the sand described above. Up to about 25 % water, the two factors change in opposite senses, with κ at a low value and changing relatively slightly, but above 25 % water both factors increase together resulting in a rapid growth of diffusion coefficient. Rough "irrigation" experiments (see Fig. 5) with initially dry sand in sectioned glass tubes qualitatively confirmed this conclusion, the slowly moving and steep water-front reflecting slow diffusion for moisture contents up to about 25 %. This figure also justifies the neglect of the gravity term excepting where the diffusion coefficient is in any case high. We do not wish to dismiss hysteresis as an agent in maintaining a long-lived moisture gradient,[21] but to emphasise the existence of another factor which does not involve recognising such a gradient as a case of static equilibrium.

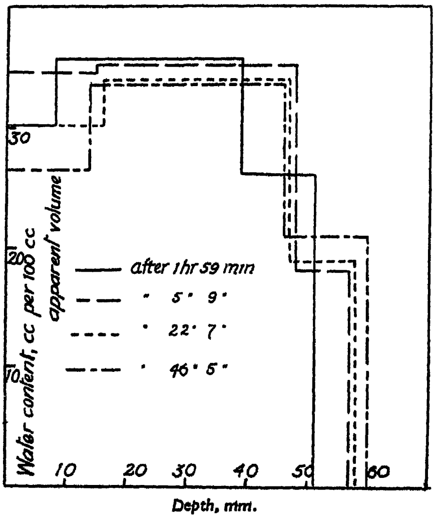

FIG. 5.—Moisture distribution in a sand column at various times after "irrigation." The initial water intake, with water front advancing to about 5 cm., took place in only 7 sec.

Others of the moisture "constants" (e.g., wilting point) seem to fall either in the group which includes field capacity, being characterised by inherent importance, explicability in terms of more-or-less understood factors, but impossibility of precise definition; or into a group characterised by precise definition in arbitrary terms, and including, for example, the hygroscopic capacity, the "*p*F 4·2 point," the moisture equivalent and the recently introduced 15 atm. and ⅓ atm. points. These latter "constants" often owe their existence to the fact that, whilst capable of reproducible laboratory determination, they approximate to certain significant but indefinable constants of the first group.

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[21] Schofield, *Trans. 3rd Int. Congr. Soil Sci.*, 1935, 2, 37.

THE THERMO-OSMOSIS OF LIQUIDS THROUGH POROUS MATERIALS

By H. P. Hutchison, I. S. Nixon and K. G. Denbigh

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I. Historical

In 1941 Derjaguin and Sidorenkov[1] published some remarkable results on the thermo-osmosis of water and other pure liquids through a sintered-glass filter. The present paper is concerned with an attempt to repeat the Russian work, together with some general remarks on the history and theory of thermo-osmosis.

The phenomenon of thermo-osmosis was discovered and named by Lippmann[2] in 1907. In his experiment a volume of water was separated into two parts by means of a membrane. When the two regions of the system were held at different temperatures, it caused a flow of water through the membrane from the cold to the hot side. Using a membrane of gelatine a few cm. in diameter the rate of flow was of the order of 50 mg./min. for a temperature difference which was of the order of 80° c.

Lippmann's work was greatly extended by Aubert[3] who made a detailed investigation of the thermo-osmosis of water and other liquids through various membranes. It was found that membranes of gelatine, pig's bladder, etc., gave rise to a flow of water from the cold to the hot side, whilst certain other membranes, notably parchment paper and viscose, gave a flow in the reverse direction. Porous plugs composed of mineral material gave no flow. Aubert found that the effect depended both on the imbibition by the membrane of some of the liquid and on the presence in the membrane of water-soluble substances. It was not the passage of these substances into the water on either side which caused the phenomenon and it only occurred whilst these substances were still *within* the membrane. Aubert concluded that the phenomenon was electrical in its origin and was related to electro-osmosis. Freundlich,[4] in his discussion of the effect, suggests that there is a membrane potential which is dependent on temperature and is thus unequal on the two sides.

If a sufficient hydrostatic pressure is applied to the part of the system towards which the flow takes place, the flow can be brought to a stop. This condition of the system, in which there is a steady difference of temperature and pressure but no flow of the liquid, will be referred to as the stationary state. Aubert found it difficult to investigate this state, due to instability, but he quotes the following figure for a particular gelatine membrane in water: pressure difference 1235 mm. water for a temperature difference which was probably about 80° c. The effect is clearly one of considerable magnitude.

A well-known phenomenon in gases which is qualitatively analogous is that of thermal effusion, which was investigated by Knudsen. When a porous barrier separates two regions of a gas which are at different temperatures, a flow takes place from the cool to the hot region, resulting in a difference of pressure. The effect depends on the diameter of the pores in relation to the mean-free-path and is a result of molecular flow through the barrier. The mechanism of the effect is known from kinetic theory and it does not allow of the possibility of flow in the reverse direction, such as had been observed in the thermo-osmosis of liquids.

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[1] Derjaguin and Sidorenkov, *Compt. rend., U.R.S.S.*, 1941, **32**, 622.

[2] Lippmann, *Compt. rend.*, 1907, **145**, 104, 105.

[3] Aubert, *Ann. Chim. Physique* (8), 1912, **26**, 145, 551.

[4] Freundlich, *Colloid and Capillary Chemistry* (1926), p. 272.

The work of Lippmann and Aubert seems to have been largely forgotten and when the fountain-effect in He II (i.e., its flow through a capillary under the influence of a temperature gradient) was discovered, it was regarded as entirely new. However, in his paper on the theory of He II, Landau [5] remarks that " the presence of the thermo-mechanical effect is not in itself peculiar only to helium, anomalous is only the large value of the effect." In pursuance of Landau's remark, Reekie and Aird [6] investigated the possibility of a thermo-mechanical (i.e., thermo-osmotic) effect in water by establishing a temperature gradient across a porous plug of material such as French Chalk. It was concluded that if any such effect exists it is less than 10^{-4} of that observed in helium. This result is in agreement with that of Aubert, who had found no thermo-osmosis of water through plugs of inorganic material. It was therefore very surprising when Derjaguin and Sidorenkov [1] reported a very considerable effect when a temperature gradient was created across a sintered-glass disc immersed in water, carbon tetrachloride and other liquids.

Reekie and Aird, and also Derjaguin and Sidorenkov, seem to have been unaware of the earlier work of Lippmann and Aubert. At the same time London [7] and other workers on the theory of the fountain-effect make no mention of a thermodynamic treatment of thermo-osmosis which had been given by Eastman,[8] and later by Wagner.[9] This thermodynamic treatment, which has been recently extended by de Groot,[10] shows in brief that a thermo-osmotic effect is to be expected, provided that the transport of fluid across the barrier involves a certain heat effect. This heat effect is the absorption of heat on the one side of the barrier and its liberation on the other, and must be assumed to take place even if the two sides are at the *same* temperature. The thermodynamic treatment then comprehends the following phenomena : (*a*) thermal effusion in gases, (*b*) the fountain-effect in He II, (*c*) the thermo-osmosis of liquids. (We are not aware of any corresponding observable effect in pure solids.) The thermodynamic treatment tells us nothing about the mechanism of the effect, which is, no doubt, different in these three cases.

The origin of the present paper was an attempt to repeat the experiments of Derjaguin and Sidorenkov. At the same time we have sought to clarify the rather confused situation described above as a preliminary to a more extensive investigation which we have in hand.

II. Repetition of the Experiments of Derjaguin and Sidorenkov

The apparatus used by the Russians is shown diagrammatically in Fig. 1 *a*. D is a sintered-glass disc, of average pore diameter 10^{-4} cm., C is a horizontal capillary, H a heating coil and S a stirrer. The liquid under investigation filled the vessel up to a meniscus in the capillary. The procedure adopted was to heat the liquid in the main part of the vessel over a period of 50–100 sec. without stirring. Since the vessel was cylindrical, this heating did not upset the hydrostatic balance. The heating was then discontinued and the stirrer was set in motion. This caused heated liquid to reach the upper surface of the sintered-glass disc. There was an immediate shift of the meniscus towards the right and the rate of this movement was observed and recorded. It was found to be approximately proportional to the temperature difference across the plate (10–40° c.) and for different liquids the magnitude of the effect was in the following order: $CH_3{\cdot}OH > CCl_4 > CH_3{\cdot}COOH >$ water $>$ 0·1N. NaCl in water. For water the initial linear rate of flow was of the order of 10^{-2} cm./sec. for 1° c. temperature difference and for methyl alcohol it was about five times larger. The Russian authors do not quote the diameter of their capillary and the volume rate of flow is, therefore, not known. They found also that the deposition of oleic acid within the pores of the disc caused a reduction of the effect with water by approximately two times.

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[5] Landau, *J. Physics, U.R.S S.*, 1941, **5**, 71.
[6] Reekie and Aird, *Nature*, 1945, **156**, 367.
[7] London, *Proc. Roy. Soc. A.*, 1939, **171**, 484.
[8] Eastman, *J. Amer. Chem. Soc.*, 1926, **48**, 1482 ; 1927, **49**, 794 ; 1928, **50**, 283.
[9] Wagner, *Ann. Physik* (5), 1929, **3**, 629 ; 1930, **6**, 370.
[10] de Groot, *Physica*, 1947, **13**, 555 ; *Compt. rend.*, 1947, **225**, 173.

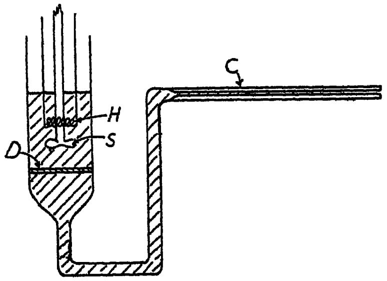

Fig 1*a*

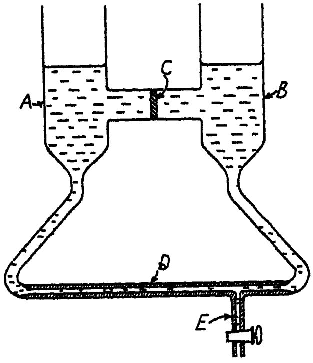

Fig. 1*b*

The present authors constructed a similar apparatus and observed movements of the meniscus in the capillary (0·075 cm. diam.). It became evident, however, that there were several sources of error which are not mentioned by the Russians in their paper. One of these was the evaporation from the surface of the water in the main part of the vessel and this was overcome by covering it with a layer of Apiezon oil. However, a more serious difficulty was the discovery that the temperature of the water *below* the disc began to rise immediately the heated water reached the upper surface. It seemed that the movements observed in the capillary might be due entirely to the slow heating and expansion of the water below the disc, i.e., a thermometer effect. This was confirmed when it was found that an apparatus containing a *solid* glass plate, in place of the porous disc, gave an initial linear rate of movement in the capillary of about 10^{-2} cm./sec. for 1° c. difference of temperature, which is the same as that obtained by Derjaguin and Sidorenkov and which they regard as due to thermo-osmosis. However, in view of the uncertainties as to the relative diameters of capillaries, etc., there still remained the possibility of a genuine thermo-osmosis, over and above that part of the movement observed by the Russians which we believe to be due simply to thermal expansion.

The present authors therefore constructed a second apparatus in which heat was supplied at a constant rate at one side of a sintered-glass disc and was removed at a constant rate at the other side. By creating a stationary temperature gradient, in place of a transient one, effects due to thermal expansion, and resultant pressure changes, are avoided and the thermo-osmosis, if it is present, should be observable as a continuous flow.

The apparatus is shown in Fig. 1 *b*. The two vessels A and B are connected by a transverse tube in which is sealed the porous disc C, 2 cm. diam. and 0·3 cm. thick. The vessels were connected at the bottom by means of a capillary D, 1·47 mm. diam. which was kept horizontal. A side arm E in the capillary made it possible to introduce a bubble of air in order to indicate any return flow of liquid from one vessel to the other, as a result of thermo-osmosis. In the transverse tube to the left of the porous disc there was a small resistance heater contained in a glass tube filled with oil. A thermo-junction on either side of the porous disc was used for the measurement of the temperature difference. The whole apparatus was immersed in a thermostat at a temperature of 25° c. in order to obtain a constant rate of removal of heat. The temperature differences across the disc which were employed were of the order of 2–10° c.

Preliminary experiments were carried out with a sintered-glass disc of porosity grade 4 (pores $5\text{–}10 \times 10^{-4}$ cm. diam.). Distilled water was the liquid which filled the vessel and its surface in the two vessels was covered with a layer of Apiezon oil, in order to eliminate evaporation. The movement observed in the capillary was almost negligible, amounting to 0·046 cm. in 2½ days, for a temperature difference of 5·8° c.

More prolonged experiments were carried out with a disc of porosity grade 5 (average pore diameter 10^{-4} cm.). Using water in the vessel, rates of movement of the order of 3×10^{-3} cm./sec. per 1° c. difference of temperature were at first recorded and in a direction indicating a flow through the disc from the warm to the cold side. After careful re-cleaning of the apparatus, the movement was not greater than 2×10^{-4} cm./sec. per 1° c. Over two days' running of the apparatus, the rate of this movement declined and eventually became a very slow movement (10^{-5} cm./sec. per 1° c.) in the reverse direction and then ceased altogether. It seemed possible that this slow decline and reversal of the effect might be due to the gradual elimination from the porous disc of traces of chromic acid used for cleaning. The apparatus was therefore again refilled with distilled water. On restarting, not the slightest movement was observable, until a small amount of chromic acid was introduced into the disc when an appreciable, but rather erratic, movement again became evident, first in one direction and then in the reverse. In each of these runs it was confirmed that there was no sticking of the indicator bubble in the capillary by observing its movement caused by the addition of a drop of water to one or other of the vessels.

As a result of the experiments, the authors are convinced that there is no significant thermo-osmosis of water through a sintered-glass disc, provided that it is entirely free from any electrolyte. We also observed no movement when carbon tetrachloride was used as the liquid under investigation. Experiments were also carried out on water in which the porous-glass disc was replaced by a tightly packed plug of activated carbon. An initial flow was observed in the direction from cold to warm. This flow eventually reversed itself and finally became zero. The initial flow may have been due to the ions of the activating substance in the carbon.

III. Thermodynamic Conditions for the Appearance of Thermo-osmosis

The experiments described above show that the thermo-osmosis of water through a sintered-glass disc is a negligibly small effect. Similar conclusions with regard to thermo-osmosis through plugs of chalk, etc., had been described previously by Aubert, and by Reekie and Aird. The apparent thermo-osmosis through sintered-glass described by Derjaguin and Sidorenkov we believe to be due to the thermal expansion of the liquid, or to the presence of impurities. It remains to consider under what conditions a true thermo-osmotic effect may appear; some information on this question is available from thermodynamics.

The type of system which we are considering is not at equilibrium since there is a temperature gradient and a flow of heat. It is therefore unsuitable for discussion by the methods of classical equilibrium thermodynamics (" thermostatics "). For this type of problem two methods of treatment have been used.

(*a*) The method known as " quasi-thermostatic." This was first used by Kelvin[11] in his treatment of the thermo-electric effect and by Helmholtz[12] for the case of the concentration cell with transport. The method has been applied by Eastman[8] and Wagner[9] to several types of processes, including thermo-osmosis, in non-isothermal systems. The essential features of the method are: (1) the assumption that the equilibrium condition of the second law, $\Sigma \mathrm{d}S = 0$, can be applied at the stationary state of the system, to those parts of the process which are assumed reversible, despite the simultaneous occurrence of processes, such as heat conduction, which are not reversible; (2) the assumption of a " heat of transfer." The nature of these assumptions will become clearer from the following treatment which is similar to that of Eastman.

Consider two vessels, I and II, containing the same pure substance, and which are in complete thermodynamic equilibrium with each other. Each vessel is in contact with a heat reservoir and both are at the same temperature T. If the substance is in *different* phases in the two vessels, the reversible transfer of material between them will involve absorption of latent heat, L, in the one vessel and its liberation in the other. However, the overall entropy change for the reversible transfer is

$$\mathrm{d}S_r + \mathrm{d}S_s = 0 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where the subscripts r and s refer to the reservoir and to the substance respectively. By applying this equality we can then obtain the Clausius-Clapeyron equation,

$$\mathrm{d}p/\mathrm{d}T = L/T.\Delta V \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If the substance is in the *same* phase in the two vessels, we are not normally accustomed to regard this reversible transfer between the vessels as involving any heat, simply because it is not necessary to allow for it. For example, if the transfer is effected by passage through a membrane there may be heat absorbed, Q^*, when the substance dissolves in the membrane at the one side and the liberation of the same amount of heat when the substance passes out of the membrane at the other side. Since the temperatures are equal, the two entropy terms, $-Q^*/T$ and Q^*/T, exactly cancel and are therefore not usually considered. However, in the case of non-isothermal systems, the two entropy terms do *not* cancel. The heat effect, Q^*, must then be allowed for and is the origin, in a thermodynamic sense, of phenomena such as thermo-osmosis.

The heat of transfer, Q^*, is then defined as the heat absorbed in vessel I and liberated in II when one mole of the substance is transferred from I to II by a particular mechanism, the temperatures and pressures remaining constant. The magnitude of Q^* depends on the mechanism of transfer, e.g., through a porous plug, membrane or capillary, and may be zero.

Consider now the thermo-osmotic system consisting of the same pure substance in two vessels I and II at temperatures T and $T + \mathrm{d}T$ and pressures p and $p + \mathrm{d}p$. Each vessel is in contact with a heat reservoir at temperatures T and $T + \mathrm{d}T$ respectively. The transfer of one mole of the substance from I to II involves an entropy increase *in the substance* given by

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[11] Kelvin, *Mathematical and Physical Papers*, Vol. I, p. 232 *et seq.*

[12] Helmholtz, *Wied. Ann.*, 1878, **3**, 201.

$$\mathrm{d}S_s = \left(\frac{\partial S}{\partial T}\right)_p \cdot \mathrm{d}T + \left(\frac{\partial S}{\partial p}\right)_T \cdot \mathrm{d}p \quad . \quad . \quad . \quad . \ (3)$$

There is a simultaneous change of entropy of the reservoirs due to the heat of transfer, Q^*. The entropy increase in the two reservoirs is given by

$$\mathrm{d}S_{r_1} = \frac{Q^*}{T + \mathrm{d}T} - \frac{Q^*}{T} = -\frac{Q^* \cdot \mathrm{d}T}{T^2} \quad . \quad . \quad . \ (4)$$

There is a second entropy change, $\mathrm{d}S_{r_2}$, in the reservoirs due to the heat absorbed by the substance in the change of state from T, p to $T + \mathrm{d}T$, $p + \mathrm{d}p$. This entropy change is given by

$$\mathrm{d}S_{r_2} = -\frac{1}{T}(\mathrm{d}U + \mathrm{d}w) = -\frac{1}{T}\left\{\mathrm{d}U + (p + \mathrm{d}p)\left(V + \frac{\partial V}{\partial p}\cdot \mathrm{d}p + \frac{\partial V}{\partial T}\cdot \mathrm{d}T\right) - pV\right\}$$

$$= -\frac{1}{T}\left\{\left[\frac{\partial U}{\partial p} + p \cdot \frac{\partial V}{\partial p} + V\right]_T \mathrm{d}p + \left[\frac{\partial U}{\partial T} + p \cdot \frac{\partial V}{\partial T}\right]_p \mathrm{d}T\right\} \quad . \ (5)$$

At the stationary state of the system, i.e., when the temperatures and pressures are constant, it is now assumed that the following condition holds, despite the occurrence of heat conduction between I and II :

$$\mathrm{d}S_s + \mathrm{d}S_{r_1} + \mathrm{d}S_{r} = 0 \quad . \quad . \quad . \quad . \ (6)$$

Hence, from (3), (4) and (5),

$$\left[\frac{\partial S}{\partial p} - \frac{1}{T}\frac{\partial U}{\partial p} - \frac{p}{T}\frac{\partial V}{\partial p} - \frac{V}{T}\right]_T \mathrm{d}p + \left[\frac{\partial S}{\partial T} - \frac{1}{T}\frac{\partial U}{\partial T} - \frac{p}{T}\frac{\partial V}{\partial T} - \frac{Q^*}{T^2}\right]_p \mathrm{d}T = 0 \quad (7)$$

Substituting the well-known values for $\left(\frac{\partial S}{\partial p}\right)_T$ etc., eqn. (7) reduces to

$$-\frac{V \,.\, \mathrm{d}p}{T} - \frac{Q^* \,.\, \mathrm{d}T}{T^2} = 0,$$

$$\text{or } \frac{\mathrm{d}p}{\mathrm{d}T} = -\frac{Q^*}{VT} \quad . \quad . \quad . \quad . \ (8)$$

where V is the molar volume of the substance. The temperature difference $\mathrm{d}T$ will thus give rise to a pressure difference $\mathrm{d}p$, only when Q^* is not zero. The thermo-osmosis thus depends entirely on the existence of the heat of transfer.

The relation (8) is analogous to the Clausius-Clapeyron equation, (2), and is obtained by an essentially similar method. It was obtained also by Wagner, who used a cyclic method, and by London for the special case of the fountain-effect in He II. (In London's treatment it is not assumed that the heat effect is necessarily the same at either end of the capillary.)

In his original application of the " quasi-thermostatic " method, Kelvin stated very clearly that the application of the equilibrium condition (i.e., eqn. (6)) to a system through which there is a flow of heat is only a hypothesis ; ". . . however probable it may appear, experimental evidence . . . is quite necessary to prove it." Confirmation of the relations deduced from this hypothesis has been obtained in certain cases, e.g., the thermo-electric effect.[13]

(*b*) The second method for dealing with phenomena such as thermo-osmosis is that which is based on the " thermodynamics of irreversible processes," as developed by Eckart,[14] Meixner[15] and Verschaffelt,[16]

[13] See, for example, Epstein, *Thermodynamics*, p. 366.

[14] Eckart, *Physic. Rev.*, 1940, **58**, 267, 269, 919, 924.

[15] Meixner, *Z. physik. Chem.* B, 1943, **53**, 235 ; *Ann. Physik.*, 1943, **43**, 244.

[16] Verschaffelt, *Bull. Acad. Sci. Belg.*, 1942, **28**, 490.

together with the reciprocity relations of Onsager.[17] An account of its application to the fountain-effect in He II has recently been given by de Groot[10] and his treatment is valid for other forms of thermo-osmosis. The following is a brief account of the essential features of the method.

By analogy with the dynamics of mechanical systems, it is necessary, in order to develop a true "thermodynamics," to introduce velocities and forces. Thus, if a flow of heat is taking place at a rate J_1 it may be regarded as due to a thermal "force" X_1, which is dependent on the gradient of temperature. Similarly, a flow of matter at a rate J_2 is due to a "force" X_2, which is dependent on the gradient of chemical potential. If both flows take place simultaneously in the same system it may be supposed, in the absence of evidence to the contrary, that the flow rates J_1 and J_2 each depend on *both* of the forces X_1 and X_2. This is a more general assumption than its converse (i.e., that J_1 depends only on X_1, J_2 on X_2), and effects such as the thermo-osmosis and thermal diffusion depend, in fact, on the flows J_1 and J_2 *not* being independent.

As a first approximation, it is assumed that the flows are linear functions of the forces:

$$\left.\begin{aligned} J_1 &= L_{11}X_1 + L_{12}X_2 \\ J_2 &= L_{21}X_1 + L_{22}X_2, \end{aligned}\right\} \quad . \quad . \quad . \quad (9)$$

where L_{11}, etc., are coefficients. It remains to determine the form of the forces, X_1 and X_2, which were stated above to depend on the gradients of temperature and of chemical potential.

Consider a system in which is taking place spontaneous processes such as heat conduction, diffusion, chemical reaction, etc. It is a fundamental feature of the theory of Eckart and Meixner that the rate θ of creation of entropy per unit volume, due to these natural processes, is always expressible as the sum of a number of terms (one for each process), and each of these terms is the *product of two factors*. It follows that the rate of energy dissipation, which is $T\theta$, can also be expressed as the sum of products of two factors: $T\theta = \sum_i (j_i x_i)$. Now in each pair, the factor j_i can be chosen as equal to J_i, the rate of flow, or displacement, of heat, matter, etc. By analogy with the relation, work = displacement × force in mechanics, the factors x_i are therefore identified as the "forces," X_i, which give rise to the flows or displacements. Moreover the theory gives the explicit expressions for these forces in terms of the gradients of temperature, chemical potential, etc. By the use of these expressions, the eqn. (9) can then be applied to any particular problem, as, for example, thermo-osmosis.

At the stationary state of the thermo-osmotic system, we have J_2, the flow of matter, is zero, whilst J_1, the flow of heat, remains finite. Hence from (9),

$$L_{21}X_1 = -L_{22}X_2 \quad . \quad . \quad . \quad . \quad (10)$$

The substitution in this equation of the expressions for X_1 and X_2, in terms of the differentials of temperature and pressure, dT and dp, then gives the relation,

$$V\,\mathrm{d}p = -\frac{\varphi}{T}\cdot\mathrm{d}T,$$

$$\text{or } \frac{\mathrm{d}p}{\mathrm{d}T} = -\frac{\varphi}{VT} \quad . \quad . \quad . \quad . \quad . \quad (11)$$

where φ is a function of the coefficients L_{21} and L_{22} of eqn. (10). Finally, the Onsager theory gives the reciprocity relation $L_{21} = L_{12}$, and this can be used to discover the physical meaning of the function φ in (11). It is found to be equal to the energy which is transported when a mole of the substance is moved between the two halves of the system and is thus identical with the "heat of transfer" of Eastman and Wagner. The theory thus gives the same relation,

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[17] Onsager, *Physic. Rev.*, 1931, **37**, 405; 1931, **38**, 2265.

$$\frac{dp}{dT} = -\frac{Q^*}{VT} \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

as is obtained by the "quasi-thermostatic" method, but without the supposition that the system obeys the equilibrium condition of the second law. The same relation had also been obtained previously by Derjaguin and Sidorenkov[1], by using the Onsager relations, but we have not been able to follow the details of their treatment.

To sum up, it seems that (12) can be obtained by a number of different methods of a thermodynamic type. It is a relation which gives the difference of pressure, as a function of the difference in temperature, between the two parts of a system composed of a single fluid substance. It is evident that the pressure difference is only obtained when the particular mode of separation of the two parts of the system is such that the heat effect Q^* is not zero. For example, in the thermal effusion of gases, Q^* is finite and is due to a change in the average energy of the molecules when the motion changes to molecular flow in the pores of the barrier.[9 18 20] The value of Q^* can then be calculated and it has been shown by Wagner[9] and Casimir[18] that eqn. (12) reduces to the same expression as is obtained by kinetic theory for thermal effusion and is in agreement with experiment. In the case of the fountain-effect in He II, the heat effect seems to be due to a difference in properties between superfluid and normal helium. The experimental results of Meyer and Mellink[19] are again in good agreement with eqn. (12).

For thermo-osmosis through membranes the heat Q^* is presumably related to the heat of solution of the fluid in the substance of the membrane. A rough "explanation" of the thermo-osmotic effect may then be given as follows. If the heat of solution is finite, the solubility will vary with the temperature, according to classical thermodynamics. The amount of the fluid dissolved in the membrane will thus tend to be unequal on its two sides, and there will be a concentration gradient within the membrane which results in a continuous flow of the dissolved substance from one side to the other.

It is possible, however, that no case of thermo-osmosis through membranes due solely to the heat effect Q^* has yet been found. Thus, in many of the examples described by Lippmann and Aubert, there was strong evidence of an electro-kinetic mechanism arising from the presence of impurities within the membrane. As regards the thermo-osmosis of water and other liquids through sintered-glass discs, Derjaguin and Sidorenkov attribute the effects observed by them to a change in the specific heat of the liquid in very thin layers close to the surface of the glass. However, the results of our own repetition of their work show that the effect, if it exists, must be very small indeed. It remains to discover, therefore, a case of thermo-osmosis through membranes or porous barriers, other than the thermal effusion of gases at low pressures, on which the thermodynamic relation (12) can be tested. Alternatively, it may be possible to extend the thermodynamic treatment to include the effect of electro-kinesis.

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[18] Casimir, *Rev. Mod. Physics*, 1945, **17**, 343.

[19] Meyer and Mellink, *Physica*, 1947, **13**, 180, 197.

[20] Herzfeld and Smallwood, in Taylor's *Treatise on Physical Chemistry*, 2nd Ed., p. 199.

Summary

A survey is made of the history and theory of the thermo-osmosis of water and other fluids through porous material. The authors have repeated certain experiments of Derjaguin and Sidorenkov in which it was claimed that there is a significant thermo-osmosis of water and other liquids through a sintered-glass disc. The present work shows that the effect with water and carbon tetrachloride is entirely negligible provided that care is taken to avoid effects due to thermal expansion and to the presence of electrolyte. Thermodynamic analysis suggests that a necessary condition for the thermo-osmotic effect is the existence of a certain " heat of transfer " across the porous barrier. In the case of a sintered-glass disc, it seems that this heat effect must be negligible.

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GENERAL DISCUSSION

Mr. S. Baxter (*Wrexham*) (*communicated*) : I would like to comment on one point in Prof. Adam's introductory remarks. The value of 120° quoted by Baxter and Cassie for the advancing angle of water against a wool fibre cannot be taken as a true contact angle as the fibre itself has a rough surface. Further Wenzel's equation is not valid for a water-repellent wool yarn as there is not a continuous solid-water interface. The porous surface equation must be applied and this is rendered difficult due to film formation between fibres when the water is receding from the yarn. Unless the area of water film formed can be determined the f values for the yarn cannot be obtained. For a water-repellent yarn we have

$$\cos \theta^1_A = f_1 \cos \theta_A - f_2 \quad . \quad . \quad . \quad . \quad (1)$$

$$\cos \theta^1_R = f_1 \cos \theta_R - f_3 + f_4 \quad . \quad . \quad . \quad . \quad (2)$$

and

$$f_3 + f_4 = f_2 \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Where the θ's, f_1 and f_2, are as defined earlier,[1] f_3 is the area of air-water interface and f_4 the area of water-water interface per unit geometrical area of yarn surface when the water is receding from the yarn. It is clear that an independent estimate of, say, f_4 is necessary for a solution of the equations.

Dr. S. J. Gregg (*Exeter*) and **Dr. R. I. Razouk** (*Cairo*) (*communicated*) : In eqn. (1) of Prof. Adam's paper, it is not explicitly stated whether γ_s is the free surface energy of the clean solid, i.e. exposed to vacuum, or of the solid carrying an adsorbed film. The usual practice is to take it as the free surface energy of the clean solid γ_{SO}; eqn. (1) then becomes

$$W_{SL} = (\gamma_{SO} - \gamma_{SL}) + \gamma_{LV} \quad . \quad . \quad . \quad . \quad (a)$$

In eqn. (2), however, γ_s refers to the solid carrying an adsorbed film (formed by adsorption from the vapour phase or by spreading from liquid or both) and is perhaps more clearly written γ_{SV}; for eqn. (2) this gives

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta \quad . \quad . \quad . \quad . \quad (b)$$

The distinction between γ_{SO} and γ_{SV} in relation to contact angles is implicit in Harkins and Dahlstrom's paper of 1930,[2] but was first made explicit by Bangham and Razouk in 1937.[3]

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[1] Cassie and Baxter, *Trans. Faraday Soc.*, 1944, **40**, 546.

[2] Harkins and Dahlstrom, *Ind. Eng. Chem.*, 1930, **22**, 897.

[3] Bangham and Razouk, *Trans. Faraday Soc.*, 1937, **33**, 1459.

At constant temperature, γ_{SL} and γ_{LV} are fixed but γ_{SV} is dependent on the amount adsorbed Γ and is in principle calculable from the Gibbs adsorption isotherm [4]:

$$\gamma_{SV} = \gamma_{SO} - \int_0^p \Gamma RT \, d\ln p \quad . \quad . \quad . \quad . \quad (c)$$

where Γ is the adsorption in mol. cm.$^{-2}$ and p the pressure of vapour. From eqn. (*b*) and (*c*), $\cos\theta = f(\Gamma)$ and this shows clearly the marked influence of the adsorbed film on the contact angle.

Consider first the case where impurities are rigorously excluded: this entails removal of grease and such-like contamination, thorough outgassing to the degree usual in vapour adsorption measurements, and conducting the experiment in an enclosure containing only the solid, the experimental liquid and its saturated vapour, with complete absence of air.

When advancing contact angles are being measured, if the adsorption is rapid, γ_{SV} falls quickly to its limiting minimum value for the saturated vapour pressure, viz. γ°_{SV}, and the contact angle rapidly rises to its equilibrium value given by

$$\cos\theta_e = (\gamma^{\circ}_{SV} - \gamma_{SL}) / \gamma_{LV} \quad . \quad . \quad . \quad . \quad (d)$$

If, however, the adsorption equilibrium is attained slowly, the contact angle will rise from a low initial value and reach its maximum value θ_e only after some time. This state of affairs, where the *advancing* contact angle *increases* up to a maximum could be but rarely encountered in practice, however, for the experimental conditions are extremely exacting.

In measuring the receding contact angle, the vapour-saturated surface has to be flushed with the liquid. As the latter recedes, the film remaining on the surface is duplex in nature: its upper surface has the properties of the bulk liquid and therefore gives zero contact angle. Such a film is unstable (except when the contact angle is zero) [5] and its energy relation is given by

$$\gamma_{SL} + \gamma_{LV} = \gamma_{SL} + \gamma_{LV}\cos\theta_r \quad . \quad . \quad . \quad . \quad (e)$$

so that $\cos\theta_r = 1$. Comparing with eqn. (*d*), $\gamma_{SL} + \gamma_{LV} > \gamma^{\circ}_{SV}$, since $\cos\theta_e < 1$. In other words, the duplex film has higher free surface energy than the adsorbed film formed from the saturated vapour and is therefore unstable relative to it. Consequently the duplex film converts spontaneously into an adsorbed film so that the contact angle must increase from its zero value, ultimately reaching the equilibrium value θ_e. Clearly a change of structure is involved from that of bulk liquid to that of the adsorbed layer; and a conversion of this kind requires time, and moreover might pass through a number of intermediate states, each giving rise to a different contact angle. Thus, unless sufficient time is allowed, pseudo-equilibrium values of the contact angle less than θ_e would be obtained, i.e. there is hysteresis of the contact angle.

In presence of impurities the conditions are altered. Of particular interest is the case when the surface is contaminated with a substance which is so tenaciously adsorbed that it is displaced only very slowly by the vapour of the liquid ($\gamma_{SF} < \gamma_{SV}$), though prolonged contact with the liquid may remove it. If γ_{SF} is the free surface energy of the contaminated surface, the advancing contact angle will be given by

$$\cos\theta_a = (\gamma_{SF} - \gamma_{SL}) / \gamma_{LV}$$

and will be greater than the equilibrium contact angle, since $\gamma_{SF} < \gamma_{SV}$. The receding angle will be given by

$$\cos\theta_r = \frac{(\gamma_{SFL} + \gamma_{LV}) - \gamma_{SL}}{\gamma_{LV}},$$

where γ_{SFL} is the interfacial free energy of the contaminated surface against the liquid, soon after flushing. In general, γ_{SFL} will differ very little from γ_{SF} and in most cases, therefore, $\gamma_{SFL} + \gamma_{LV} > \gamma_{SF}$, so that $\cos\theta_r > \cos\theta_a$ i.e. the receding angle is less than the advancing angle.

This picture is not based on any particular mechanism of adsorption or particular shape of isotherm as in Dr. Cassie's theory. The effect described will, of course, be additional to other causes of hysteresis of the contact angle such as the roughness of the surface or its inhomogeneity.

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[4] Bangham, *Trans. Faraday Soc.*, 1937, **33**, 805.

[5] Harkins, *J. Chem. Physics*, 1941, **9**, 552. Cp. *Colloid Chemistry*, (ed. Alexander, 1946), **6**, p. 61.

Dr. W. Hirst (*Aldermaston*) (*communicated*) : In eqn. (1), (2), and (3) of his paper, Prof. Adam has (*a*) assumed that the surface free energy and surface tension of a *solid* can be equated, and (*b*) ignored the adsorbed film which at equilibrium, is necessarily present on the solid.

(*a*) Gibbs[6] [7] has pointed out that the surface tension of a solid—the force required to increase the surface by stretching it, i.e. by a process which keeps the number of surface atoms unchanged—is not, in general, numerically equal to the surface free energy—the work required to produce additional surface *of the same nature as before*. It is, therefore, desirable to use different symbols to denote the two quantities. If γ is retained to denote surface tension, F (the usual symbol for the Helmholtz free energy) may appropriately be used to denote surface free energy.

(*b*) If a solid and liquid are in equilibrium, the liquid is also in equilibrium with its saturated vapour ; it follows that there is on the solid an adsorbed film in equilibrium with the saturated vapour. It is important to note also that when a film is adsorbed, the changes in surface free energy and surface tension are not, in general, numerically equal ; only when the adsorbed film is mobile can the changes be equated.

Thus, for eqn. (1) and (2) to be generally valid, they should read,

$$W_{SL} = F_{SV} + \gamma_{LV} - F_{SL} \quad . \quad . \quad . \quad . \quad (1)$$

$$F_{SV} = F_{SL} + \gamma_{LV} \cos \theta \quad . \quad . \quad . \quad . \quad (2)$$

where F_{SV} = the free surface energy of the solid in equilibrium with the saturated vapour. The use of γ (as defined above) instead of F tacitly assumes that the adsorbed film is mobile.

When the adsorbed films are mobile, the film possesses a spreading force and it becomes particularly easy to visualise the process of penetration into a capillary. Using eqn. (5) in Prof. Adam's paper, one sees that the total driving force is

$$\frac{2\gamma \cos \theta}{r} \times \pi r^2 = 2\pi r \gamma \cos \theta$$

i.e. it is the difference between the spreading forces of the two films. This seems to offer a more satisfactory way of regarding penetration than does the conception of a "penetrating pressure" of magnitude $2\gamma \cos \theta / r$ because (*a*) it emphasises that the rate of penetration will depend on whether the adsorbed vapour film has had time to form, and (*b*) it does not set an upper limit $2\pi r \gamma$ to the driving force.

It will be noted also that when the capillaries are so narrow that $\gamma \cos \theta$ loses its meaning, the difference between the spreading forces of the two films may alter but it has still a definite meaning.

Prof. N. K. Adam (*Southampton*) (*communicated*) : I am glad to learn that Mr. Baxter ascribes the rather large advancing angle on a wool fibre, of 120°, in part to a roughness factor. Ablett's value of 113° therefore seems the largest reliable value. The value of 105° for paraffin wax, quoted in *The Physics and Chemistry of Surfaces*, p. 186, is not the advancing angle, but the mean between advancing and receding angles, and is very nearly Ablett's figure.

Dr. Gregg, Razouk, and Hirst, suggest that I have ignored the adsorption of vapour on the solid surfaces in the fundamental eqn. (1) to (3) of my paper. The symbols γ_s and γ_{SL} were however intended (surely this is legitimate ?) to include the cases of solid surfaces with any amount of adsorbed vapour on them. Of course the actual values of the surface free energies of solids vary with the amount of vapour adsorbed on them, and the appropriate values must be substituted in my equations. I do not think these equations are wrong, but they are sufficiently general to cover solid surfaces with much adsorbed vapour or with practically none.

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[6] *Collected works*, 1928, 1, 315.

[7] Bangham, *Trans. Faraday Soc.*, 1937, **33**, 805.

I have not, as Dr. Hirst says, "assumed" that the force required to stretch a solid surface *without changing the number of surface atoms* is numerically equal to the surface free energy. I have chosen, as I and many others have done for a long time (although some recent critics seem not to have realised this), to use the words "surface tension" for the free surface energy. This may seem to Dr. Hirst a crime, but there it is! It seems to me debatable whether the force required to stretch a surface without altering the number of surface atoms, i.e. without equilibrium between surface and interior being established, is a sufficiently definite, or in principle measurable, quantity to merit being called by the familiar name "surface tension," despite Gibbs' use of the term "superficial tension" for it. Gibbs very neatly distinguishes between these quantities as the work required to *stretch* a solid surface, and the work required to *form* a new surface. I prefer to use "surface tension" for the latter quantity, Dr. Hirst assumes that the words "surface tension" mean the latter quantity. I feel that a discussion on the precise meaning to be assigned to the familiar words "surface tension" may be desirable, but that can scarcely be done here.

Dr. W. Hirst (*Aldermaston*) (*communicated*): Prof. Adam has made clear the sense in which he used the words "surface tension." It is unfortunate that some authors use "surface tension" when referring to the work of *formation* of a new surface, whereas others regard it as the work of *stretching* a surface. I strongly support his suggestion that a discussion should be held to decide on the terminology to be used in future.

Mr. S. Baxter (*Wrexham*) (*communicated*): As the present Discussion is very much concerned with contact angles and surface structure, some measurements I carried out some time ago, whilst with the Wool Industries Research Association, on the contact angles shown by wax surfaces against water are interesting.

The advancing contact angle of water against paraffin wax is generally taken to be approximately 106° and the receding angle approximately 95°.[8] [9] [10] Ablett,[11] however, quotes values somewhat higher, namely 113° and 96°. Differences in contact angle for a given substance can easily arise due to roughness and porosity of a surface [1] and it seemed useful to investigate these effects for paraffin wax and spermaceti. Microscope slides were coated with the two waxes by heating the slides and then allowing a small quantity of the wax to melt and run over the surface of the slide. After cooling, the slides were examined under a microscope to get an idea of the surface structure and then their contact angles against water were determined by placing a drop of water on the slide and tilting until the drop was on the point of moving. A photograph was then taken and after suitable enlargement the contact angles could be readily measured. The two surfaces in this state were extremely rough, due to the contraction of the waxes on solidification, the effect being much greater for the spermaceti. Flat surfaces of the two waxes were then prepared by compressing a slab of wax against a piece of plate glass for a long period. On detaching, the wax had an extremely flat finish and showed excellent reflecting properties. Contact angles for the two waxes were then measured and are compared with the values for the rough surfaces in the table below.

	Paraffin Wax		Spermaceti	
	Advancing	Receding	Advancing	Receding
Rough surface	110°	89°	118°	89°
Smooth surface	97°	89°	83°	37°

The values show the extreme importance of surface structure and enable the values of f_1 and f_2 to be calculated. (f_1 is the area of solid-water interface and

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[8] *International Critical Tables.*

[9] Summer, *Wetting and Detergency* (Harvey, 1937), p. 41.

[10] Adam, *Physics and Chemistry of Surfaces*, 3rd ed. (Oxford), p. 186.

[11] Ablett, *Phil. Mag.*, 1923, **46**, 244.

f_2 is the area of water-air interface per unit geometrical area of the rough solid-water interface.[1]) The result is for paraffin wax, $f_1 = 2{\cdot}57$ and $f_2 = 0{\cdot}028$, and for spermaceti, $f_1 = 0{\cdot}720$ and $f_2 = 0{\cdot}556$, whereas for the flat surface $f_1 = 1{\cdot}0$ and f_2 is zero. In the case of paraffin wax, it is seen that little air is trapped between the drop and the surface and so in this case Wenzel's equation would apply. For the spermaceti, however, the value of f_2 is quite considerable and the trapped air can be clearly seen by the internal reflection taking place from the lower surface of the drop.

It is clear from the above measurements that difference in surface structure can easily explain the discrepancies that occur in the literature for contact angle measurements of paraffin wax. The results also indicate that many contact angle measurements have little fundamental value.

Prof. N. K. Adam (*Southampton*) said: One cause of low receding angles, and therefore of hysteresis, is soaking of the liquid into the solid to an appreciable depth. A gradual decrease in the contact angle, as the time of contact with liquid increases, is very common, and is probably due to some such penetration. I find it difficult to believe that roughness alone is the principal cause of hysteresis; hysteresis occurs on polished or varnished surfaces, and I have observed at least 60° hysteresis on varnished surfaces. I doubt if these are much "rougher" than liquid surfaces.

Dr. D. J. Crisp (*Cambridge*) said: Dr. Cassie's suggested mechanism to explain the difference between the advancing and receding angle of contact of a drop on a plane surface is based essentially on the assumption that the only accessible state of aggregation of molecules adsorbed from the vapour is a cluster at a single localised site, while different states of aggregation are accessible to the surface left by the retreating liquid.

The true equilibrium state should include the possibility of every kind of molecular arrangement, whether in large or small clusters, and all these states should be included in deriving an expression for the entropy of the adsorbed molecules. If this were done, there would be in general only one value for the adsorption and only a single distribution of molecular aggregates representing the equilibrium state. Hence it follows that either the surface over which the drop advances, or the surface at the rear of the drop, or both, are not in complete equilibrium with the vapour.

If we accept that the difference in contact angle is due, not to a change in the solid-liquid interface, but to a change in the solid-vapour interface, it is possible to show that the dis-equilibrium of one of the surfaces will be accompanied by a difference of vapour pressure of the adsorbent in the regions immediately preceding and succeeding the moving drop. It appears to be impossible to have two surface states of adsorbent with identical vapour pressures but different surface energies, as is required by Cassie's treatment.

Applying the Neumann triangle of forces and employing superscripts to denote advancing and receding edges and subscripts to denote solid, liquid and vapour (air) interfaces :—

$$\gamma^{A}_{SL} + \gamma^{A}_{LA}\cos\theta^{A} - \gamma^{A}_{SA} = \gamma^{R}_{SL} + \gamma^{R}_{LA}\cos\theta^{R} - \gamma^{R}_{SA} \quad . \quad . \quad (1)$$

Since $\gamma^{A}_{LA} = \gamma^{R}_{LA} = \gamma_{LA}$, and by hypothesis, $\gamma^{A}_{SL} = \gamma^{R}_{SL}$,

$$\gamma_{LA}\,(\cos\theta^{R} - \cos\theta^{A}) = \gamma^{R}_{SA} - \gamma^{A}_{SA} \quad . \quad . \quad . \quad . \quad (2)$$

The Gibbs adsorption equation is now applied to any small difference between γ^{R}_{SA} and γ^{A}_{SA} thus :

$$-\,d\gamma_{SA} = \Gamma_{S}d\mu_{S} + \Gamma_{L}d\mu_{L} + \Gamma_{A}d\mu_{A} \quad . \quad . \quad . \quad (3)$$

By suitable definition $\Gamma_{S} = 0$, and since $d\mu_{A} = 0$ (air)

$$-\,d\gamma_{SA} = \Gamma_{L}d\mu_{L} = \Gamma_{L}\,.\,RTd\log p_{L}{}^{*} \quad . \quad . \quad . \quad (4)$$

It follows from (2) and (4) that if adsorption is positive the vapour pressure of the adsorbate at the rear of the moving drop is less than at the front; if adsorption is negative, as might occur on a hydrophobic surface, the vapour pressure is raised behind the drop. In either case, a process of distillation would be possible to complete the thermodynamic cycle and recover the work,

$$\gamma_{LA}(\cos\theta^{R} - \cos\theta^{A}).$$

If adsorption is very high, eqn. (4) indicates that a relatively large change in γ, and therefore in contact angle, would be possible with a small degree of disequilibrium in vapour pressures.

The application of the phase rule to an adsorbing surface[12] also predicts, in general, only one adsorbed phase in equilibrium with the vapour, except at a singular pressure or temperature where two phases co-exist. In such a case, however, although the amount adsorbed in the two phases is different ($\Gamma_1 \neq \Gamma_2$) the vapour pressures and interfacial tension are identical ($d\mu = d\gamma = 0$)

It is important to note that no thermodynamic difficulties are involved in Shuttleworth and Bailey's explanation[13] since the *real* contact angle is considered to be the same on either side of the drop, the observed angle being spurious.

Dr. A. B. D. Cassie (*Leeds*) said: In reply to Dr. Crisp, clusters of all sizes are taken into account for both the advancing and receding surfaces, but their distributions are different because the potential energy of the molecules is different in the two cases: in fact, states which are accessible to molecules in the receding surface are inaccessible to those adsorbed on the dry surface. Experimental adsorption hysteresis shows that this must be true. This hysteresis also shows that different amounts of water—whether or not as distinct phases—can be adsorbed at one vapour pressure. These experimental data can only be reconciled with the ordinary surface relations given by Dr. Crisp if one pursues the conception of a heterogeneous surface to the limit of molecular dimensions. This is what I have attempted to do, and I assume, as do Shuttleworth and Bailey. that the "real" contact angle with the dry surface is the same on either side of the drop; the "irregularities" on my surface—the clusters—are, however, different on the two sides of the drop.

Mr. R. Shuttleworth (*Bristol*) said: It appears that further progress in the understanding of contact angle hysteresis must await experiments planned to distinguish between the various theories. Hysteresis is in some cases caused by the initial presence of foreign adsorbed molecules; and perhaps the hysteresis when spreading occurs on liquid mercury, as noted by Dr. Kemball, is of this nature.

I am not, however, convinced by Dr. Cassie's arguments which seek to explain hysteresis by adsorption on the solid of molecules from the liquid. On a smooth surface the contact angle is given by Dr. Cassie (eqn. (2)) in which γ_{SA} is the only quantity affected by adsorption; γ_{SA} is less than the surface energy of the clean solid by an amount nF where F is the mean free energy of adsorption per liquid molecule and n is the number of adsorbed molecules per unit area. The contact angle increases with increase of nF. Dr. Cassie suggests that at an arbitrary temperature two different configurations of adsorbed molecules can exist in equilibrium on different portions of the solid, each with exactly the same value of F. This seems implausible; I feel there must be a single configuration which has an absolute minimum of free energy of depth F_1, and that Dr. Cassie's two identical values are not real but arise from the crudity of the assumptions he makes in his numerical argument.

It is perhaps possible that a more refined argument would show that there are two unequal minima of depths F_1 and F_2; and that at an arbitrary temperature there can exist two different configurations of adsorbed molecules, in stable and metastable equilibrium. If the first configuration occurred on the solid before the advancing liquid and the second configuration on the solid uncovered by the receding liquid, in order to explain hysteresis it would be necessary to show that $n_1F_1 > n_2F_2$ (advancing greater than receding contact angle). It is to be expected that it is the second configuration, which arises from recession, that is metastable ($F_1 > F_2$). However, it is also probable that $n_1 < n_2$, that is, there is adsorption hysteresis. Although contact-angle hysteresis always occurs, there seems no obvious reason why, for the metastable configuration, the greater value of n_2 should always be more than compensated by the smaller value of F_2. In a complete treatment it would also be necessary to show that the spontaneous change from the metastable to the stable configuration is a process taking a number of hours.

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[12] Crisp, *Trans. Faraday Soc.* and *J. Chim. Physique.* (Bordeaux Meeting, 1947)
[13] Shuttleworth and Bailey, this Discussion.

Dr. A. B. D. Cassie (*Leeds*) said: In reply to Mr. Shuttleworth, although the theory is semi-quantitative, the experimental fact of adsorption hysteresis shows that at least two configurations must give one minimum or two close minima of free energy. Any theory, however crude or exact, must give this result.

Dr. C. Kemball (*Cambridge*) said: I should like to suggest that it is possible to have a multimolecular layer in the form of a continuous film which would have a finite contact angle with the parent liquid. This suggestion is contrary to one of the conclusions of Cassie's paper. Dr. Cassie has indicated that he believes the difference between the surface film in contact with the saturated vapour and the three-dimensional liquid is only one of distribution of the adsorbed material—there being isolated patches of liquid on the surface as postulated by the B.E.T. theory. I suggest that the nature of the multimolecular film may be entirely different from the three-dimensional liquid—the outer layer being, in many cases, continuous and either gaseous or of a liquid character but not identical with the bulk liquid. There are undoubtedly systems where a continuous second, and possibly a third and fourth, layer will form on a uniform surface at vapour pressures less than the saturation pressure. If the heat of adsorption of the vapour to this second layer is greater than the heat of condensation and the loss of entropy no greater, there will be the necessary decrease in free energy for the second layer to form. However, this outer layer may well be gaseous, which would mean that the work of adhesion of the liquid to it will be less than the cohesion of the liquid. This would give a finite contact angle in the presence of a continuous multilayer. In other cases the outer layer might have a liquid nature and yet not be identical with the three-dimensional liquid—again giving rise to a finite contact angle.

Dr. W. Hirst (*Aldermaston*) (*communicated*): Dr. Cassie regards adsorption as taking place on a number of localised sites sufficiently separated to allow distinct molecular clusters to be adsorbed at each site. This type of adsorption cannot be general, for experimental evidence often opposes such an explanation. Bangham,[14] Gregg [15] and, later, Harkins and Jura[16] have directed attention to the fact that if molecules adsorbed on solid surfaces are treated as possessing lateral mobility, there is a strong resemblance between the equations of state which then result and the equations of state of films adsorbed on liquid surfaces. Secondly, if the adsorbed molecules are mobile the underlying solid will be stretched. Maggs [17] has measured this stretching for a charcoal-methanol system and he also measured the mechanical properties of the charcoal. He was able to show that the stretching force was approximately equal to that which would be exerted by a film with a spreading force equal to the surface free energy lowering. The result almost certainly rules out the possibility that the dimensional changes on adsorption of the film arose merely from a rearrangement of the intermolecular forces within the adsorbent; the evidence strongly supports the hypothesis that the films were mobile. Finally, Hill [18] has shown theoretically that, for the adsorption of common vapours at room temperature, mobility may be expected to be the rule rather than the exception.

Harkins and Jura [16] have observed a first-order transition in the low-pressure region of the adsorption isotherm of heptane on ferric oxide, and in other adsorption isotherms. This kind of transition occurs only when there exists an appreciable energy of interaction between adjacent adsorbed molecules. In this system therefore, if localised sites exist, they are close together.

It is clearly a limitation of the derivation of the B.E.T. equation by statistical mechanics that adsorption on localised sites is postulated and that the contradictory hypothesis has then to be made that the partition function γ_L of a molecule in the second and higher layers is identical with that of a molecule in the bulk liquid. Furthermore, the postulate that the interaction energy between an adsorbed molecule and the molecule immediately above it is equal to E_L is artificial; for cubic packing a more appropriate value would be $E_L/3$, or $E_L/2$ for hexagonal close packing. The heat of adsorption would only rise to the latent heat of the liquid when the number of horizontal neighbours sufficed to provide the necessary interaction energy. This observation suggests that the B.E.T. equation would predict too great an amount adsorbed— which at high vapour pressures it often does; the peculiar feature is that, at fairly low pressures whilst the second layer is filling, the assumption in the B.E.T. theory that the heat of adsorption is equal or nearly equal to the latent heat of the bulk liquid does, in fact, often yield an adsorption isotherm in good agreement with experiment. A question requiring answer is therefore—why does the use of $E_L/3$ (or $E_L/2$) instead of E_L lead to worse agreement with experiment in the low-pressure region of the isotherm?

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[14] Bangham and Fakhoury, *J. Chem. Soc.*, 1931, 1324.

[15] Gregg, *J. Chem. Soc.*, 1942, 696.

[16] Harkins and Jura, *J. Amer. Chem. Soc.*, 1946, **68**, 1941.

[17] Maggs, *Trans. Faraday Soc.*, 1946, **42B**, 284.

[18] *J. Chem. Physics*, 1946, **14**, 441.

It is possible that the assumption that the values of the partition function γ_L and the potential energy term E_L are the same as for a molecule in the bulk liquid may lead to serious error. The writer wishes to emphasise that detailed molecular pictures such as Dr. Cassie (having at his disposal a wealth of other experimental evidence) has drawn for the adsorption of water by keratin, should not be drawn for other systems without similar supporting experimental evidence.

Dr. A. B. D. Cassie (*Leeds*) (*communicated*): In reply to Dr. W. Hirst, there are no fundamental differences between a B.E.T. isotherm derived by statistical mechanics and one derived from evaporation-condensation arguments; both postulate localised sites, but statistical mechanics has shown how multimolecular isotherms can arise with mobile monolayers.[19] [20]

There appears to be a great desire to abandon the hypothesis of localised adsorption, and doubtless many phenomena, such as spreading pressures, can be more easily visualised with mobile monolayers, but it should not be forgotten that localised monolayers exhibit very similar spreading pressures.[21] On the other hand, there are two elementary empirical phenomena associated with many forms of adsorption which have not been reconciled with the properties of a mobile monolayer. The two phenomena are that many examples of adsorption do give measurable vapour pressures when adsorbed largely as a monolayer, and they also show a large heat of wetting for the dry adsorbent; differential heats of wetting of around 3000 cal./mole are quite common. If this amount of heat is evolved, the vapour pressure, p, in equilibrium with the adsorbate must be given by an expression of the form:

$$\frac{p}{p_0} \sim \frac{j_L}{j_a} e^{-\omega/RT}$$

where p_0 is the saturation vapour pressure of the adsorbate, j_L is the liquid partition function of its molecules, j_a is its adsorbed partition function, and ω is the differential heat of wetting, in this example 3000 cal./mole. The order of magnitude of p is given by this relation for any adsorption, be it multimolecular, monomolecular, localised or mobile. At 300° K., the equation shows that $p \sim 6 \times 10^{-3} p_0$ unless j_a is less than j_L; or the observed vapour pressure will be negligible unless j_a is less than j_L. As we know that the vapour pressures of adsorbates are comparable with their saturation vapour pressures, there seems to be no escape from the conclusion that j_a is very much less than j_L. But if we postulate a mobile monolayer, j_a must be greater than j_L, and only by assuming strong localisation for the monolayer can j_a become much less than j_L. This is the argument that has led me to conclude that adsorption isotherms which are associated with large heats of wetting must be localised so far as the monolayer is concerned; in fact, the localisation must be so strong as almost to constitute a chemical bond. There are, of course, examples where a heat of wetting is absorbed, and a mobile monolayer is then possible,[1] but such examples are rare amongst published data.

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[19] Cassie, *Trans. Faraday Soc.*, 1945, **41**, 456.

[20] Hill, *J. Chem. Physics*, 1947, **15**, 767.

[21] Fowler and Guggenheim, *Statistical Thermodynamics* (Cambridge, 1939), p. 443.

Dr. D. H. Bangham (*B.C.U.R.A., London*) said: In view of the large number of papers written on the subject of adsorbed water it is astonishing how little experimental work is directed towards ascertaining its *properties*. Most writers are content with being able to give a self-consistent account of a very small range of facts of which more than one explanation is possible. There are, however, awaiting solution a number of technical problems which turn upon the behaviour of these films, and it is important that their nature should not remain merely a matter of conjecture.

One example is that of the mutual adhesiveness—or stickiness—of dust particles in a gas stream that contains water vapour. Although at all but very low relative humidities each dust particle is enveloped by a film of water molecules, it is certain that the particles do not behave like water droplets. The common-sense solution—adopted by engineers—is that dusts (even hydrophilic ones) are non-adhesive as long as the gas is kept above the dewpoint. This state of affairs fitted in very well with Langmuir's no-longer-tenable conception of a single chemisorbed water monolayer. It is difficult to harmonise with the now-established fact that near saturation the layers are multimolecular and mobile unless we agree that the film constitutes a phase with distinctive properties different from those of the bulk liquid.

I agree with Dr. Cassie in suggesting that the difference is one of entropy (or configuration) rather than of energy. I believe there are a number of cases where the curve of adsorption against relative humidity is nearly temperature-independent near saturation, and this implies an adsorption energy very close to the normal latent heat. Moreover, by exposing clean surfaces (such as freshly split mica) to *supersaturated* vapour one can build up the adsorbed films to *visible* thickness and still demonstrate their non-identity with the bulk liquid, drops of which refuse to *spread* on the film. I do not agree with Dr. Cassie that the configurational difference can lie in the formation of immobile clusters, because the experiment shows that the visible film exerts a lateral pressure, often sufficient to drive the drop away.

It is important to recognise that these relatively thick films, even on dust particles, do not *necessarily* provide nuclei of condensation of normal liquid water.

Dr. W. W. Barkas (*Princes Risborough*) said: Since this section of the Discussion is concerned with the fundamental aspects of the subject I should like to make a few observations on some of the points raised in the preliminary papers where, it seems to me, very simple fundamental considerations may not have been kept sufficiently in mind.

SURFACE TENSION.—A surface is a geometrical abstraction and not a physical reality. Thus, on a molecular scale, the surface of a liquid is a transition region between the bulk liquid and its vapour. Thermodynamic deductions apply to homogeneous phases and are valid only on a much larger scale where molecular dimensions are negligible.

Surface tension arises from asymmetry in the cohesive forces of a liquid at points close to its boundary and it involves a transition layer of appreciable but indefinite thickness between the liquid and its vapour. Thus surface tension is expressed as dynes/cm. instead of, like any other stress, as dynes/cm.^{2}, because we know the area, but not the volume of the surface layer or how the energy is distributed within it. When Prof. Adam discusses the possible change of surface tension of liquid in a tube which is small compared to the range of molecular forces, he is dealing with a case where the thickness of the transition region and the amplitude of thermal agitation are large compared with the diameter of the tube. The term "surface tension," therefore, ceases to have any real meaning, since the surface cannot be defined on the scale of accuracy required by the problem.

The Kelvin equation, used in calculating the curvatures of a meniscus from the vapour pressure, is similarly limited in application to large capillary spaces. One cannot build a meniscus out of only a few molecules, nor can one surround them with a cylindrical tube of definite radius. Thus, on a scale where the Kelvin equation is applicable, the question of whether or not to allow for the thickness of the adsorbed layers becomes irrelevant since the thickness of a layer of two or possibly even ten molecules on the walls of the capillary would be quite negligible.

In the calculation of the distribution of capillary radii the Kelvin equation can be misleading, even where the capillaries are reasonably large, unless the voids in the solid form a system of orderly circular tubes, and this for two reasons. Firstly, the volume occupied by the meniscus itself will not, in general, be of a simple geometric shape and the amount of water removed, following a small drop in vapour pressure h, will depend on the change in this shape as well as on the change in cross-section of the capillary. Secondly, where very many short capillary spaces are involved, instead of a few long ones, the error due to neglecting the total volume of the menisci may become large and cannot be determined. For a circular capillary, this error is equivalent to a tube length of $\frac{2}{3}r$ at *each* meniscus, so it is evident that the error will be appreciable when the length of each capillary is small enough to be comparable with the radius.

SWELLING.—If the capillary is reasonably large the liquid water held under a concave meniscus is under hydrostatic tension (hence the reduced vapour pressure). There is thus no possibility of *liquid* water causing a separation of molecular layers by "forcing its way" between them. The swelling resulting from the adsorption of moisture by the solid phase must be a molecular phenomenon and is not concerned with surface tension of the liquid. It is true that an increase in the adsorption of capillary water, if accompanied by a *rise* in vapour pressure, may cause an increase in the external dimensions of a porous solid, since the hydrostatic tension in the water decreases with increased vapour pressure. This may be looked upon as a "swelling" but it is, I think, better described as a volume increase due to the release of capillary stresses, because if the increase in capillary sorption occurred at a *constant* vapour pressure it would cause a further shrinkage due to the increased area over which the constant tension would be acting.

Mr. K. J. Nieuwenhuis (*Delft*) (*communicated*) : Dr. Barkas* criticized Prof. Adam's considerations about the surface tension of a liquid in a capillary, which is so narrow that the range of attraction of the walls extends even to the middle of the capillary (Fig. 2 of Prof. Adam's paper). Dr. Barkas felt that the number of molecules in the surface layers of the liquid within such a capillary is too small so that a statistical calculation of a mean value of the excess free energy of the liquid in the surface layers over the free energy of the liquid in bulk would not be possible.

However, it should be borne in mind that statistical mean values can be calculated, either by considering the (large number of) molecules present in a large surface area at one single moment; or by considering the (likewise large number of) molecules entering into a rather small surface area and disappearing again from it during a certain lapse of time.

Therefore it is not impossible to speak about the surface tension of a liquid within such a very narrow capillary, providing that the "time of observation" of the liquid surface is long enough with regard to molecular events (which can still appear to be very small to human experience). The narrower the capillary is, the longer the period will be over which the excess potential energy of the molecules in the surface layers and the probability of their arrangement, i.e. the free energy of the surface layers of the liquid, should be averaged.

Moreover, in general, the downward attraction of the solid walls below the level XY of the surface molecule A (again Fig. 2 of Prof. Adam's paper), and the upward attraction of the walls above XY will not cancel each other in a vertical direction. The forces of attraction can be van der Waals'—London (dispersion) forces, and also electrical forces, arising from the interaction between ions and dipoles of the substances involved. These two types of forces of attraction are the smaller, the higher the dielectric constant of the medium through which they are working. The dielectric constant of any liquid is greater than that of its vapour and also than that of air; in general, it is greatest with substances of a highly polar nature. For instance in the formulæ for the van der Waals'—London (dispersion) forces the dielectric constant for liquid water has a value of about 2;

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* This Discussion, p. 105.

as far as electric (polar) forces are concerned, the dielectric constant of liquid water has a value between 5 and 80, depending on the distance over which these forces are working.

This means that with any liquid the downward attraction of the solid walls below the level XY of the surface molecule A is smaller than the upward attraction of the walls above XY, so that the decrease in surface tension caused by the bore of the capillary being very small, is still greater than would be expected from the considerations in Prof. Adam's paper.

That part of the decrease in surface tension in a very narrow capillary which was mentioned by Prof. Adam will be appreciable, when the radius of the capillary is smaller than the "radius of the sphere of attraction" of one liquid molecule towards other liquid molecules. This second cause of a decrease of the surface tension is appreciable when the radius of the capillary is smaller than the radius of the "sphere of attraction *via* vapour (or air)" of a molecule in the capillary wall above the surface of the liquid, towards the liquid molecules (which is the same as the radius of the "sphere of attraction *via* vapour (or air)" of a liquid molecule towards molecules of the solid which builds the material of the capillary walls).

Another case, which can be dealt with, is the surface tension of a liquid layer spread over the walls of a very narrow capillary. If the capillary is long compared with molecular dimensions, we then do not have to average over a certain lapse of time, but we can simply consider all the molecules present in the surface layers at one moment, and average over the rather large surface area considered. If the diameter of the space not occupied by liquid within the capillary is smaller than the "radius of the sphere of attraction of one liquid molecule towards other liquid molecules *via* the gas or vapour phase," the surface tension of the liquid film must be smaller than that of a liquid film of the same thickness in a wider capillary.

However, this does not necessarily mean that spreading of the liquid over the walls of a very narrow capillary will occur more readily than in a wider capillary, because it would be accompanied by a greater decrease in free energy (per unit surface area of the walls), and therefore would take place more rapidly. In a very narrow capillary, opposite sides of the walls can also be attracting each other before the liquid is introduced, so that the free surface energy of the solid can be smaller in such a very narrow capillary than in a wider one.

No general answer is possible to the question, whether spreading of a liquid over the walls is favoured by a very small bore of the capillary. Only quantitative or semi-quantitative calculations, based on the actual dimensions of the capillary and on the specific properties of the substances constituting the liquid and the solid, can give the answer in each single case.

The same applies to the influence of a very small bore of a capillary on the penetration pressure, p_i. For a cylindrical capillary without constrictions we can write:

$$p_i = \frac{2\gamma_L \cos \theta_A}{r} \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

where the influence on θ_A of a very small diameter of a capillary is not exactly known.

Eqn. (*a*) is equivalent to:

$$p_i = \frac{2(\gamma_S - \gamma_{LS})}{r} \quad . \quad . \quad . \quad . \quad . \quad (b)$$

where γ_S = free surface energy per unit surface area of the solid (walls of the capillary), and

γ_{LS} = free interfacial energy per unit interfacial area at the interface liquid-solid.

Eqn. (*b*) merely states that the penetration pressure is proportional to the decrease in free energy of the system capillary + liquid, occurring when liquid penetrates into the capillary. Detailed considerations show, that in some cases this decrease can be greater in a very narrow capillary than in a wider one (in both cases taken per unit surface area of the capillary walls, of course); but in other cases the reverse will be true. However, the direct effect on the penetration pressure of a very small radius of a capillary is much greater, as the radius itself occurs in the denominator of (*a*) and (*b*).

It should be remarked, that the general principle underlying eqn. (*b*) is also valid, when spreading of the liquid over the capillary walls takes place with greater speed than penetration by filling of the capillary, so that liquid penetrates into a capillary the walls of which have already been wetted. If the capillary is wide and the liquid in the middle of the capillary can be considered to be identical with ordinary liquid in bulk, the decrease in free energy occurring when the capillary is filled with liquid, is determined only by the free surface energy (surface tension) of the originally present liquid film. The last-mentioned surface tension is smaller in the case of a very narrow capillary.

However, with a very narrow capillary the number of liquid molecules going into the interfacial layers of the liquid is smaller, if the interfacial layers of the liquid, extending from the walls of the capillary, are overlapping, so that there is no bulk liquid present in the middle of the capillary filled with liquid. Then, in going into the capillary, fewer liquid molecules have to be separated from part of their neighbours in the bulk state. The consequence of this would be a greater decrease in free energy occurring in filling an already wetted capillary with liquid, if the bore of the capillary is very small.

Moreover, there is also possible a further decrease in the mutual attraction of the solid molecules on opposite sides of the capillary, caused by filling the capillary completely with liquid. This again would mean an increase in free energy of the system, which does not occur in a wider capillary.

Because of these opposite effects present when the bore of a capillary is very small, it cannot be said with certainty whether the decrease in free energy (per unit surface area of the wetted capillary walls) is smaller or greater with a very narrow than with a wider capillary in the case where liquid penetrates into narrow and the wide capillary the already wetted capillaries even when the liquid films on the walls of the capillaries have same thickness. (If this last condition does not obtain, the attracting forces between liquid and solid molecules also come into the picture.) Only quantitative or semi-quantitative calculations based on the actual dimensions of the capillary, and on the specific properties of the compounds constituting the liquid and the solid can give the answer.

Dr. W. W. Barkas (*Princes Risborough*) (*communicated*) : In reply to Dr. Nieuwenhuis, I was not disputing the reality of " the mean value of the excess free energy of the liquid in the surface layers over the free energy of the liquid in bulk." On the contrary, in any arbitrary volume in the surface region of Prof. Adam's fine capillary, an energy difference must exist and might be calculable on a statistical time basis as he suggests. My plea was that the term " surface layers " is undefined—how many layers, or what volume, is required to constitute a surface ? We might take too thin a layer and obtain a large energy difference since only the most "abnormal" molecules were included, or too thick a layer and find a small difference since too large a number of " normal " molecules were included.

Later in his communication Dr. Nieuwenhuis in connection with "a very small bore of a capillary," mentions " the decrease in free energy per unit surface area of the wetted capillary walls." If the capillary is of near molecular dimensions, we must decide what " surface " we are to take through a ring of thermally agitated molecules before we can determine the free energy *per unit surface area*. Arbitrary decisions could lead to enormous differences in the calculated surface area of a capillary of near molecular dimensions. In this problem too, how many layers of molecules are to be included in the estimate of the decrease in free energy ?

Dr. R. K. Schofield (*Harpenden*) said : Desorption curves obtained originally by van Bemmelen, and subsequently by Foster and other investigators using systems having pores somewhat smaller than those of the ferric oxide gel of Foster's Fig. 1 frequently exhibit a large loss of sorbate for a very small fall in vapour pressure. It has occurred to me that in these cases the main controlling factor is the tensile strength of the liquid. The cohesion in liquids is several thousand atmospheres and so is of the right order of magnitude. The absence of hysteresis in gels with still smaller pores may perhaps be attributed to the limited tensile strength of liquids.

Dr. A. G. Foster (*Englefield Green*) said: Prof. Adam's suggestion that γ is lower in a narrow capillary would make the radii, calculated by the Kelvin equation using the normal value of γ, too high. I think there is probably an increase in V (the molecular volume) in small pores, where the liquid is under tension, which may compensate for the decrease in γ and possibly maintain the product $V\gamma$, which enters into the Kelvin equation, at approximately its normal value.

Dr. Cassie points out that the statistical interpretation of multimolecular adsorption leads to the idea of clusters. There is, however, no reason why the first layer should not be continuous. Capillary condensation leads to a decrease in free energy only when the surface is already covered with an adsorbed layer.[22] If parts are covered and parts bare, there may no longer be a net decrease in free energy when a pore is filled. Present theories of multilayer adsorption being derived for plane surfaces cannot be expected to hold without modification for porous solids since they fail to consider the curvature of the surface, which *increases* with increasing thickness of the absorbed layer. I have pointed out elsewhere [23] two factors which tend to assist adsorption beyond the first layer on a curved surface: (1) the potential does not fall off so rapidly with distance, and (2) the "cylindrical meniscus effect" produces a lowering of free energy which is approximately half that due to capillary condensation in a pore of the same size. This idea has subsequently been applied to my own theory of sorption hysteresis [24] by Cohan [25] who points out that once a second layer forms by this mechanism, the pore will automatically fill completely. If the average size of the clusters required by statistical theory is about 5, this would provide an alternative mechanism for blocking small pores and initiating capillary condensation. The magnitude of the free-energy decrease associated with the cylindrical meniscus effect is $\sim$ 200–500 cal./mole, which is about the same as that due to the configurational entropy. Dr. Cassie's conclusion that the receding contact angle will not have a unique value seems to me to provide an additional argument against Zsigmondy's explanation of sorption hysteresis in terms of hysteresis of the contact angle, since the experimental facts are (*a*) the descending branch of the hysteresis loop is quite reproducible and (*b*) at corresponding volumes the radii calculated from ascending and descending curves are in no way related. Messrs. Bond, Griffiths and Maggs quote me as saying that no sign of condensation could be detected with water on silica gel. It is true that no visible condensation of liquid water on the gel was observed in this particular apparatus, but in other types of apparatus I have observed condensation of liquid water on the gel. In contrast with the behaviour of charcoal under similar conditions the gel is wetted by the water. The authors also quote my observation that water adsorbed on silica gel shows no evidence of freezing even at −65° C. but fail to mention my observation of a definite lowering of f.pt. of dioxan adsorbed on ferric oxide gel. My own interpretation of this work was that the lowering of f.pt. was inversely proportional to the pore radius of the gel and was therefore much larger on silica than on ferric oxide. I certainly still regard the water-silica gel system as an example of capillary condensation but would agree that the behaviour of water on coals and charcoal cannot be interpreted in this manner. Sigmoid isothermals are obtained with water on charcoals which give Langmuir curves with organic liquids. Since the unimolecular adsorption accounts for the whole uptake of the latter, the pore radius of these charcoals must be of the order 5–10A, so that it is not surprising that the adsorbed phase differs from ordinary three-dimensional liquid. The real difficulty is to explain why water gives an isothermal so different in shape from the normal Langmuir type. The fact that the curves are convex to the p axis even at low pressures could be accounted for by the B.E.T. theory if the heat of sorption were zero,[26] but the flattening out at $p/p_0 \sim 0{\cdot}5$ resembles the critical condensation phenomena first discussed by Fowler,[27] examples of which have recently been described by Harkins *et al.*,[28] but at much lower relative pressures.

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[22] Polanyi, *Trans. Faraday Soc.*, 1932, **28**, 325.
[23] *Proc. Roy. Soc. A*, 1934, **147**, 137.
[24] *Trans. Faraday Soc.*, 1932, **28**, 645.
[25] *J. Amer. Chem. Soc.*, 1938, **60**, 433.
[26] Broad and Foster, *J. Chem. Soc.*, 1945, 372.

Dr. S. J. Gregg (*Exeter*) said: Foster assumes that the adsorbed film is completely wetted by the liquid adsorbate, and puts $\theta = 0$ in the full Kelvin equation $p_d = p_0 \exp(-2V\gamma \cos\theta/rRT)$. Experimental evidence shows however that this assumption is frequently not justified: recent careful investigations by several workers (including Foster himself) show that the adsorption isotherm both on porous and on non-porous adsorbents, often intersects the line $p = p_0$ at a definite angle, giving a strictly limited uptake at p_0 and signifying that $\theta > 0$; if the contact angle were zero the isotherm would, of course, approach p_0 asymptotically. Thus, even when, according to the capillary condensation theory, the pores are completely filled with liquid, the latter gives a finite contact angle with the bulk liquid and so cannot be identical in structure with the bulk liquid. The point at issue would appear to be: is the difference between the adsorbed film and the bulk liquid a minor one which can be allowed for by regarding the film as a slightly modified liquid with somewhat different surface tension and density, as Foster implies; or, is it so great that it is no longer useful to discuss the film in terms of a bulk liquid model?

There is much to be said for this latter view. In the first place (as I pointed out some time ago[29] and as speakers at this Discussion have emphasised) it is difficult to assign a meaning to surface tension in a meniscus with a breadth of half a dozen or so molecules. This point has been made in another way by Guggenheim[30] who shows that interfacial or surface tension becomes indeterminate unless the thickness of the layer is small compared with its radii of curvature; he shows that in practice this means that in measurements of interfacial tension the results become independent of the capillary radius only when this exceeds some 500 A.

In the second place, an alternative interpretation of isotherms with a hysteresis loop (B.E.T., Type IV) is possible: an examination of $\pi A - \pi\Sigma$ curves[31] and of the plot[32] of β/Σ against $\pi\Sigma$ suggests that the loop corresponds to a transformation (probably of diffuse first-order) *within* a monolayer consisting either of single or of associated molecules (π = surface pressure of film; A = area occupied per adsorbed molecule; Σ = internal area of adsorbent; β = "two-dimensional" compressibility of film). Actually, these isotherms show a *second* turn-away from the p-axis at pressures close to p_0; and it is possible that this, and not the hysteresis loop, corresponds to the process whereby the adsorbed layer thickens until it fills the whole cross-section of the pore. Even then it would not be true liquid, as shown by the existence of the finite contact angle.

Mr. R. L. Bond (*B.C.U.R.A., London*) said: Several speakers have described methods of determining the pore-size distribution of materials having pores considerably greater than molecular size. Since the Kelvin equation cannot be reasonably applied to the determination of the size of pores in the molecular-size range it may be useful to mention a method we have used to study the pore-size distribution of a finely ground coal char, which is a material known to have pore constrictions of molecular size. By determining the heat of wetting of the char in a number of organic wetting liquids of varying molecular size, it has been found that the heat of wetting varied with molecular size in the manner shown in the figure. We have been able to show that the heat liberated on wetting unit surface area of such a carbonaceous powder by any of the organic liquids used is approximately constant and *independent of the nature of the wetting liquid*. Hence, the variation of heat of wetting with molecular volume of the wetting liquid provides a means of estimating pore size distribution. If the relationship between area wetted and heat of wetting is known (e.g. 1 cal. is liberated on 10 m.^{2}, as determined by Dr. Bangham for the wetting of charcoal by methanol) an area distribution curve may be obtained. The first differential of the curve of area wetted against molecular volume, plotted against molecular volume, constitutes a pore-size distribution curve, similar to those described by Dr. Foster.

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[27] *Statistical Mechanics*, 2nd. ed., p. 838.
[28] *J. Chem. Physics*, 1945, **13**, 535; 1946, **14**, 117.
[29] Gregg, *J. Physic. Chem.*, 1928, **32**, 619.
[30] Guggenheim, *Trans. Faraday Soc.*, 1940, **36**, 407.
[31] Gregg, *J. Chem. Soc.*, 1942, 696.
[32] Gregg and Maggs, *Trans. Faraday Soc.*, 1948, **44**, 123.

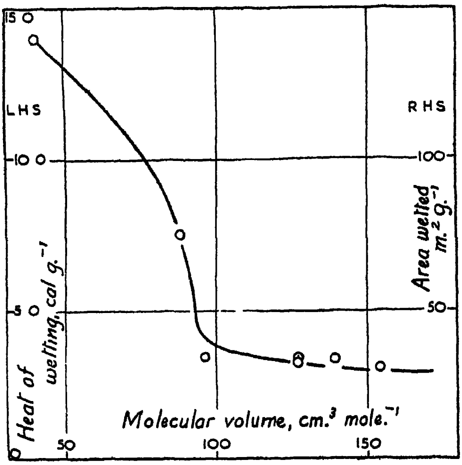

FIG. 1.—Dependence of heat of wetting and area wetted on molecular volume of wetting liquid.

Dr. W. W. Barkas (*Princes Risborough*) said : Prof. Rideal's mention of the fringed micellar structure (applicable to cellulose and other natural fibres) raises the question of the meaning of internal surface in such materials If most of the sorption occurs, as it is believed, in the disordered or amorphous regions between the crystallites, where does the surface lie ? There are indeed separate points of attachment (the –OH groups in cellulose) on which water can adsorb and between which loose chains of water molecules can form, but these do not appear to constitute surfaces I suggest it is preferable, in these materials at any rate, to look on sorption as a tendency towards the formation of a true solution which is only prevented by the anchoring of the long-chain molecules in the crystalline regions.

Equations derived to calculate the internal surfaces may, of course, be indiscriminately applied to the sorption isothermals of any hygroscopic material, such even as a sulphuric acid solution, but this does not mean that internal surfaces exist in all these cases. Such equations are most likely to be justified where the solid is porous and built up in the form of a rigid skeleton such as in charcoal. These materials show a much smaller swelling than do the natural fibres.

SORPTION ISOTHERMALS.—There is one likely reason for the limited usefulness of equations to the sorption isothermal which is not usually allowed for. This is that, in a swelling hygroscopic material at any given moisture content, the vapour pressure rises under a compressive and falls under a tensile stress by an amount which can be calculated. If, therefore, the material is subject to internal stresses during natural sorption, the isothermal will not agree with any equation, however precise, which ignores their existence. In the fringed micellæ it is difficult to see how such stresses can be avoided and their existence has been tacitly admitted by speakers who refer to water molecules " forcing their way " into the gel structure.

Dr. Cassie and others have produced some interesting reasons for supposing that Brunauer is wrong in assuming that the energy of sorption of the subsequent layers of water is equal to that of the formation of liquid water, but a much simpler reason for supposing that such water is not free is that, if this were so, it would fall out under gravity. Incidentally, equations such as the B.E.T. equation, which interprets the sorption isothermal entirely in terms of multilayer adsorption up to high vapour pressures, appear to be incompatible with the Kelvin equation which uses surface tension in the calculation of capillary radii and surface areas down to relatively low vapour pressures.

LIMITED SORPTION AT SATURATION.—Mention has been made in these Discussions of cases where the adsorption isothermal meets the saturation vapour pressure line h_0 at a finite angle instead of approaching it asymptotically. I suggest that the sensitivity of vapour pressure to stress may also help to explain this phenomenon. Thus, if in Fig. 1, OAB represents the stress-free swelling of a natural gel where the moisture content tends to an infinite value at h_0, the existence of natural restraints will mean that a higher vapour pressure will be needed to reach any given moisture content. Thus the calculated line of sorption under stress will lie along some such line as OA′B′ which is now seen to cut the saturation line h_0 at a finite angle. The upper portion of this curve A′B′ cannot be realised in practice owing to the limitations of water which cannot exist as a vapour at the higher vapour pressures.

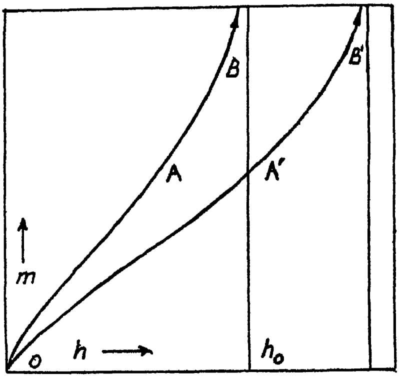

FIG. 1.

In the phenomenon of syneresis, the gel structure shrinks, so that if OAB were to represent the initial isothermal, the stress set up during shrinkage would change the isothermal to OA′B′ and all the moisture above the point A′ would condense at vapour pressure h_0 and appear as liquid water on the external surfaces, even though no capillary water were present in the gel itself.

Whatever the cause of this limited sorption, I think it is well established experimentally and cannot be put down to the fact that the true saturated vapour pressure has not been reached. When air is present in the system the rate at which equilibrium sorption is attained may be indefinitely delayed, but many experiments have been done in the absence of any gas other than water vapour, and here the entire space is always at the same absolute vapour pressure under any conditions which are reasonably static. The only local variations are those due to temperature fluctuations and these will alter the relative but not the absolute vapour pressure. In a thermostat the limitations of temperature control are such that the vapour over a free liquid surface must at times be warmer than the adsorbing solid and hence ready to condense on it, even if at other times the vapour pressure is deficient, so that on balance a hygroscopic material in such a space should be able to reach its maximum moisture content.

HYSTERESIS.—Whatever the cause of sorption hysteresis, and there may be many, the fundamental property of the sorbing material is that it suffers a work loss between adsorption and desorption and the amount of this loss can be calculated from the sorption isothermal regardless of the mechanism by which it is produced.

In defining hysteresis it is not, I think, sufficient to show that adsorption and desorption follow different paths as this is no more than an irreversible reaction. The hysteresis to be a definite property of a material must be reproducible on successive identical cycles of adsorption and desorption (Brunauer [33] makes the purely verbal mistake of using " reversible " for reproducible. The cycle cannot be reversed as this would mean a net gain of work in each cycle).

Without going into a detailed discussion of the various models which have been proposed for showing hysteresis, it is sufficient to say that if all parts of the system (i.e. the gel, its restraints and the water) are truly elastic, then either the process must be reversible or, if the model at any stage springs apart altogether due to release of stresses, then an external mechanical force, in addition to that arising from vapour pressure changes, will be required to bring them together again for a repetition of the cycle. Such a process is therefore irreversible but not reproducible in terms of vapour pressure and moisture content changes only. As a special case, McBain's " inkbottle " analogy is invalid in explaining hysteresis, as the water inside the wide bottle is unstable when put in tension by the meniscus in the narrow neck and a bubble of vapour will form in the bottle long before the vapour pressure has dropped sufficiently to empty the neck itself. This bubble will expand or collapse reversibly as the vapour pressure is lowered or raised.

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[33] Brunauer, *The Adsorption of Gases and Vapours*, Vol. 1. (Oxford University Press, 1944).

As any work loss involves irreversible or inelastic changes, the shape of the hysteresis loop will depend on the way in which changes are made (including possibly time effects also) as well as on the limits of moisture content and vapour pressure between which the cycle is performed. Thus for reproducibility a method of experiment will need to be precisely formulated. If, for example, the desorption cycle is commenced after adsorbing, from O to h_0 at A′ in Fig. 2, then the desorption curve must, of course, also start from A′ as shown by the dotted line, but if the gel be water-logged after adsorbing to A′, then the desorption curve will drop below h_0 at some much higher moisture content such as C′, and will follow a different path from h_0 and dryness. The gap between A′ and C′ can be accounted for, in the way explained earlier, by internal stresses which will affect both sides of the loop. The hysteresis loop may thus be wider at saturation than at any other vapour pressure. The path from A′ to C′ requires that water be added to the material (for example, by super saturation and condensation or by shaking in water) in order to raise the vapour pressure momentarily above its saturation value, so that the curve B′C′O is reached only with the help of some external agency and OA′C′O is not a true hysteresis loop in vapour pressure and moisture content only. It is, however, reproducible provided the same water-logged moisture content is reached on every cycle.

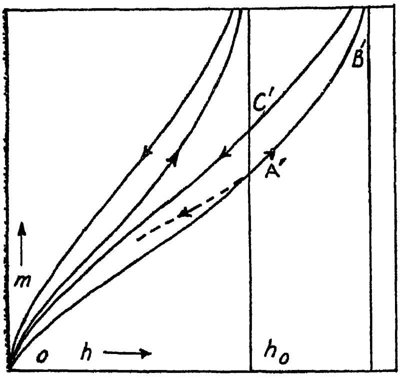

FIG. 2.

Dr. A. G. Foster (*Englefield Green*) (*communicated*) : I agree with Dr. Barkas that, on theoretical grounds, there are serious objections to the use of the Kelvin equation at low pore radii, but until the mathematical treatment of the problem can be extended to such small pores, we have no alternative but to apply the equation in its usual form and find out by experiment when and how it breaks down. We then arrive at the unexpected result that the equation appears to remain valid for comparative purposes and is remarkably successful in reducing to the same basic data for widely different liquids. Although the calculated radii are probably incorrect they are essentially of the right order of magnitude since they are consistent with the surface area determinations by independent methods.

With regard to Dr. Gregg's observations on the behaviour near saturation, it is conceivable that detailed examination in the region of 99 % saturation might show an asymptotic approach to p_0, but so far as *porous* solids are concerned, most isothermals *appear* to rise abruptly and to approach p_0 sharply. It would otherwise be possible to determine a definite saturation volume and so to establish the validity of Gurwitsch's rule for porous solids. I do not see how this saturation volume can depend on the contact angle.

The analogy between $\pi A - \pi$ curves derived from adsorption isothermals and from trough films is indeed striking, but whereas $\pi - A$ curves obtained with trough films give valuable information about molecular cross-sectional areas, no similar information has yet been provided from adsorption data treated in this way. The interpretation of adsorption data in terms of phase changes in a monolayer presents several difficulties : the cause and nature of the phase changes remain obscure ; the theory makes no quantitative or even qualitative prediction about the existence of hysteresis and there is no evidence that the saturation values correspond to the covering of a constant area rather than to the filling-up of a constant volume. The capillary theory on the other hand correctly predicts that hysteresis diminishes with increasing molecular diameter and that equal volumes are held at saturation. It is the only theory which enables us to correlate the adsorption isothermal with the structure of the adsorbent.

I agree with Dr. Schofield that the tensile strength of the liquid is an important factor. I do not regard it as the cause of the large loss of sorbate but rather as a factor determining the lower limit of capillary condensation. When condensation gives way to layer adsorption hysteresis also disappears. Dr. Barkas' comments on McBain's "ink-bottle" theory of hysteresis would appear to dispose of this explanation most conclusively.

Mr. D. K. Ashpole (*Bocking*) (*communicated*) : The small humidity cycles which Dr. Barkas points out must take place in a thermostat due to temperature fluctuations would undoubtedly at times produce supersaturation and consequent condensation within the apparatus including deposition on the hygroscopic material, but it does not necessarily follow that the hygroscopic material will attain thermodynamic equilibrium with the saturated vapour phase. Reference to Fig. 1 of my later contribution to this Discussion reveals that in the interval between 99·0 and 100·0 % R.H., a viscose sample has to absorb two-thirds as much moisture as it has already adsorbed in the range 0 to 99·0 % R.H. before it can reach equilibrium with saturated vapour. The temperature fluctuations encountered in any thermostat should be small and considerations of the relative magnitudes of the specific heat of a cellulose-water mixture and the latent heat of vaporisation of water show that a very large number of cycles would have to take place before the large amount of moisture necessary to reach equilibrium with the saturated vapour could be condensed. The occurrence of dew on the glass surfaces of the apparatus as recorded by Urquhart and Eckersall[34] will only indicate that one humidity cycle has been performed and cessation of the experiment at this point means that the hygroscopic material cannot, under any circumstances, attain equilibrium with the saturated vapour.

Mr. F. A. P. Maggs (*B.C.U.R.A., London*) said : The course of the discussion prompts one to suggest a further explanation of the rapid rise of certain isotherms at high relative pressures. Some American investigators (Emmett, in particular) have found this sharp uptake of adsorbate near saturation vapour pressures and have also observed that in some cases hysteresis is associated with this part of the isotherm. In view of the distinction between the adsorbed state and the bulk state (referred to in our paper), I would like to suggest that the form of these isotherms does not imply that the distinction is absent in such cases. The upward trend seems to me to be typical of the formation of a fresh two-dimensional phase in the adsorbed film. Dr. Gregg and I have shown[35] that such sudden changes of gradient of an isotherm are symptomatic of phase transitions *within* the film ; in some cases the occurrence of hysteresis may also be related to such transitions.

The American results have also some bearing on the observations of Dr. Barkas and Dr. Schofield since the adsorbents used by Emmett were carbonaceous solids such as carbon black, where the possibility of *plastic* deformation of the adsorbent by either film pressure or hydrostatic tension is remote.

Dr. I. W. Wark (*Melbourne*) said : It seems desirable to correct a misapprehension on the part of Bond, Griffiths and Maggs, who assume that for flotation to be possible the angle of contact must exceed 90°. Actually millions of tons of mineral are floated under conditions such that the angle of contact does not exceed 60°. The true criterion for flotation is, in fact, that the angle of contact must be finite. It should be remembered that, as Edser pointed out, the greater part of the force supporting a dense particle on the surface of water is the hydrostatic pressure of the displaced water ; the partially hydrophobic condition of the surface (as indicated by a finite contact angle) prevents the water from flowing right over the particle.

I should like to make a plea for greater use of the equilibrium contact angle. This is a physical reality for it can be approached from either direction and under appropriate conditions is quite reproducible. Reproducibility is possible, however, only for comparatively smooth surfaces, and then only if they are clean in the sense that contamination by grease or oil has been rigidly excluded. It is not easy to attain these conditions, but a satisfactory technique has been evolved in Melbourne and those laboratories in America and Europe which have adopted it have obtained contact angles that agree within 2° with the values obtained in Melbourne.

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[34] *J. Text. Inst.*, 1930, **21**, T499.
[35] *Trans. Faraday Soc.*, 1948, **44**, 123.

Unless precautions are taken to avoid accidental contamination the measured contact angles are of no value and, for this reason, many, indeed most of those reported in the literature, are misleading. Until it has been demonstrated by methods developed in connection with this work that surfaces are uncontaminated and that reproducible equilibrium angles are obtainable, I consider it futile to conduct experimental work with a view to ascertaining the cause of hysteresis. One must begin with simple systems and of these well-polished non-porous solids are the most attractive. Using such surfaces it has been found that hysteresis is much greater for a benzene-water-solid triple contact than for air-water-solid. Again in the presence of di-xanthogen which "oils" the surface, hysteresis becomes very small.

While the effects of surface roughness may not be entirely responsible for hysteresis, I have the feeling that the geometry of the system will prove to be mainly responsible in most systems. By simple diagrams it is possible to illustrate that without any change in the equilibrium angle, and taking account only of surface roughness, advancing and receding angles must differ. If we assume that in oiling the surface, di-xanthogen fills up the surface depressions it can be seen that it should reduce hysteresis.

Freedom from contamination by grease is of equal importance in measuring wetting pressures or in examining the displacement of one liquid by another from a bed of solids. Other forms of surface change such as those due to oxidation, or to adsorption or ions, are also significant. I have known measurement of wetting pressure that completely misled the experimenters because of contamination of surfaces by ions or oils. When one recalls how little matter is required to give a unimolecular film over the surface of very finely divided solids one is discouraged from approaching work of this type with light-hearted optimism. Above all it must be recognised that one cannot expose a surface to air without it becoming contaminated.

Prof. N. K. Adam (*Southampton*) (*communicated*): I do not feel sure that the existence of a finite contact angle of water on coal which, before contact with liquid water, was covered by an adsorbed film of water vapour, proves that this adsorbed film has a contact angle with water. Is it not possible, perhaps even probable, that the liquid water dissolves away this adsorbed film, itself coming into direct contact with the coal surface ? It does not seem to me justifiable to attempt to draw a dividing line between the liquid water and the water which, before immersion in the liquid, was adsorbed on the surface.

I feel a protest should be made against the suggestion in the beginning of the paper that Brunauer, Emmett, and Teller implied either identity of adsorbed layers beyond the first with bulk water, or "infinite adsorption of bulk liquid." Their theory in its general form assigns different heats of adsorption for each successive layer ; the mathematical difficulties are considerable in this general case, and for the convenience of the reader they worked out an approximate case in which the heats of adsorption for all layers beyond the first are put equal to the latent heat of evaporation of bulk water. I am not quite clear, from the paper of Bond, Griffith and Maggs, how many molecular layers were adsorbed on the coal surface ; it would seem probable that the orienting influence of the coal surface on the water molecules may extend through quite a number of layers. It is therefore not very surprising that no discontinuity in the curves of volume and dielectric constant is found, similar to that when bulk water freezes. When bulk water freezes, a peculiar rearrangement of the water molecules takes place, for which there might be neither space, nor suitable fields of force, in the comparatively thin region where water molecules are within the range of attraction either of the adsorbing solid surface, or of water molecules to which a special orientation is given by direct contact with this solid surface. One might reasonably say that the adsorbed layer is itself, to some extent, "frozen" by the act of adsorption.

Dr. D. H. Bangham (*B.C.U.R.A., London*) (*communicated*) : The statement that water has a finite contact angle against the adsorbed film refers to the film at the solid-*vapour* interface, and implies the existence of a first-order phase difference between this (saturated) film and bulk liquid water.

About the structure at solid-*liquid* interfaces we know very little, but since the interfacial layers are bounded on one side by bulk liquid it would not be surprising if they were structurally different from those at solid-vapour surfaces. If Prof. Adam means that it is unlikely there is a *first-order* change of phase on traversing from bulk liquid into the *liquid*-solid boundary layers, I would agree with him, though I would not exclude the possibility of a change of phase of the second- or third-order.

The picture of an adsorbed film as a region in which the molecules are " frozen " has grave limitations. The swelling of gels is a *dynamic* process, arising from the mobility of the adsorbed molecules. The speed with which equilibria is reached shows that water molecules can permeate coal with a rapidity inconsistent with a " frozen " adsorbed phase. This mobility is retained when the coal is cooled below 0° C.

Since, then, water adsorbed in coal (and other carbonaceous solids) is structurally different both from ice and from bulk water, it is the more important to devise experiments to ascertain its properties as Bond, Griffith and Maggs have done.

Mr. F. A. P. Maggs (*B.C.U.R.A., London*) said : I should like to take this opportunity to correct an error which appeared in the proof of the summary of our paper ; this should read that the flotation experiments show the angle of contact to be *less* than 90°.

I should like to emphasise certain general advantages which the extensometric method provides in cases where the relation between adsorption expansion and free-energy change is established. In isolating for measurement the energy changes at the solid-vapour or solid-liquid interface, other effects such as those due to gravitational forces and those arising from changes of the liquid-vapour interface are eliminated. The difficulties due to lack of stability at the solid-vapour interface (e.g. the hysteresis of the contact angle, which has been under discussion) are not encountered, as time can be allowed for full equilibrium to be reached, the steady state being detected by the length measurements.

Mr. R. L. Bond, Miss M. Griffiths, Mr. F. A. P. Maggs (*B.C.U.R.A., London*) (*communicated*) : In answer to Prof. Adam, we would remark that the identity between adsorbed film (at saturation) and bulk liquid is not merely implicit in the B.E.T. theory but is explicitly recognised by these authors. Thus they state : " If we deal with adsorption on a free surface, then at saturation pressure of the gas, P_0, an infinite number of layers can be built up on the adsorbent."[36]

We cannot accept Prof. Adam's suggestion that a different state of affairs could ensue if E_2, E_3, etc. $> E_L$, for this would lead to the paradoxical result that an increased heat of adsorption (increased, that is, in comparison with the case where $E_2 = E_3 = E_L$) would be associated with a lower (integral) surface concentration.

However, the emphasis of our paper does not lie in the film properties predicted by theory, but in the properties which we have determined experimentally, and in this respect our results oblige us to reject Prof. Adam's analogy between adsorbed molecules and " frozen " water. Any attempt to explain the increase of the coefficient of thermal expansion brought about by the adsorption of water, based on the concept of immobile " frozen " molecules must necessarily account for the dynamic phenomenon of adsorption swelling. The rate of adsorption alone is far too great with coals—and indeed with most gels—to be consistent with any theory of " frozen " adsorbed molecules (which would block the small pore entrances in the case of coal). So far from acting as immobile " frozen " units, the adsorbed films exhibit both quantitatively and qualitatively those properties to be anticipated from *mobile* adsorbed molecules exerting a 2-dimensional pressure.

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[36] *J. Amer. Chem. Soc.*, 1938, **60**, 312.

Prof. N. K. Adam (*Southampton*) (*communicated*) : On further consideration, I feel that the existence of a contact angle between bulk water and a coal surface covered by the adsorbed film in equilibrium with water vapour definitely proves that the outside of the adsorbed film has a lower work of adhesion for bulk water than the work of adhesion of bulk water to itself.

My reference to the adsorbed film as " to some extent frozen " was not intended to imply that the adsorbed molecules are immobile on the surface ; there is, I fully agree, plenty of evidence that they can move about parallel to the surface, within the attractive field of force of the surface. I am not, however, surprised that the experiments reported in the paper show that the adsorbed molecules, presumably in several superposed molecular layers, have their movements so restricted by the attraction perpendicular to the solid surface, that they are unable to rearrange themselves on cooling into the more open and very peculiar arrangement characteristic of ice in bulk. Perhaps my expression "to some extent frozen," was not very well chosen to convey this view.

Dr. A. B. D. Cassie (*Leeds*) said : Although B.E.T.'s original derivation of their isotherm suggested that the multilayers were identical with three-dimensional liquid water, the statistical derivation shows that the two forms have different complete partition functions, and are, in fact, quite different forms of water. The experimental data given by Bond, Griffith, and Maggs which require the adsorbed water to form a distinct phase are, therefore, quite consistent with a B.E.T. multilayer.

Dr. M. Joly (*Paris*) said : The films of water adsorbed on solids and the bound water in some colloidal systems produce phenomena which seem to indicate that the properties of water at an interface are different from the properties of water in bulk. One confirmation of this point of view is given by the study of the mechanical behaviour of the monolayers, Particularly in the viscosity measurements of very dilute gaseous films, for interpreting the experimental results, it is convenient to consider around each polar group of the molecules in the monolayer two or three rows of water molecules which do not show the properties of a liquid but are rigidly bound all together and with the polar group.

More generally, for all monolayers the free energy of activation of flow can be described as a sum of two terms, one ΔF_C for the film itself and the other ΔF_{H_2O} for the water molecules which are connected with it, that is to say, for the first layer of water molecules which are directly adjacent to the molecules of the organic monolayer and which are moving with it without slipping. It is possible to calculate both these terms from the van der Waals' forces if the structure is known. The figures obtained for ΔF_{H_2O} are in very good agreement with the experimental data by assuming for the water not the almost tetrahedral structure of ordinary liquid water but a hexagonal structure similar to the structure attributed to the bound water in clays. These facts indicate a change in the water structure at the interfaces.

Mr. A. Morris Thomas (*Greenford*) (*communicated*) : Bond, Griffith and Maggs report the results of measurements of the dielectric constant of wet and dry coal and are unable to find agreement with values calculated from a mixture formula. It may be taken for granted that no mixture formula is valid if there is interaction between the materials concerned, but it is surprising that the experimental values are the higher. On any hypothesis it seems unlikely that adsorbed molecules have a greater freedom than they have in the free state. It is possible that the authors have neglected the effect of the high loss angle (tan δ) which the wet coal probably possessed. The capacitance measured with a Schering bridge is the "equivalent series capacitance" and for comparison with the values estimated from a mixture formula the "equivalent parallel capacitance" must be used. The correction factor is $(1 + \tan^2\delta)^{-1}$ so that

$$\varepsilon_{\text{parallel}} = \varepsilon_{\text{series}}/(1 + \tan^2\delta).$$

When attempting to use an electrical method of this type to determine a phase change, the frequency must be carefully considered. The authors use 15 kc./s. which would probably give a measurable fall of dielectric constant for a phase change from water to ice at 0° c., but at lower temperatures the dielectric constant of ice at this frequency increases and the change becomes inappreciable.

Garton has discussed the problem of the dielectric constant of water adsorbed by cellulose.[37] As mentioned in the original paper, neglect of expansion of the cellulose on sorbing water tends to give low values and he has informed me that after taking this into account, the value obtained is between 15 and 20.

The use of measurements of electrical properties to assist the investigation of the mechanism and binding forces involved in sorption is often possible and is to be encouraged. In a large number of cases, the materials involved will be polar dielectrics and will therefore exhibit Debye resonance, i.e. there will be critical maxima in the curves of loss angle (tan δ) plotted as a function of temperature for a given frequency or as a function of frequency at a given temperature. Such maxima are related to the relaxation times of the polar groups and the effect of the sorbed substance on these values should yield important information. I am at present engaged on some work on these lines.

I am also interested in the determination of the heats of sorption. Bond, Griffith and Maggs give only one sorption isotherm and I think two or three more would be of interest. I have found that in the case of films of organic polymers containing hydrophilic groups, e.g. electrical insulating varnishes, if a moisture sorption isotherm is determined and the sorption plotted as a function of relative humidity instead of partial pressure, the curve obtained serves for any temperature in the range investigated, i.e. 20°–40° C. In the region for which Henry's law is applicable, i.e. in general up to a relative humidity of 50 or 60 %, it follows at once from this result that the heat of sorption is the same as the heat of condensation. This is presumably evidence that in these cases the sorbed molecules are probably attached to the substance by hydrogen bonds; it is certainly unlikely that the sorbed moisture exists as liquid water. The total sorption at saturation of these materials is of the order of 1–2 %, and there is no doubt that the moisture is uniformly dispersed in the bulk of the material, except for a surface film, the mass of which, however, appears to be only a small fraction of the total.

Mr. F. A. P. Maggs (*B.C.U.R.A., London*) (*communicated*): Mr. Thomas' observation regarding the low value of the net heat of adsorption of water is paralleled by measurements we have made of the integral heat of adsorption of water on a range of coals (calculated from the heat of wetting in water and the corresponding weight of water adsorbed at saturation).

The integral heat of adsorption does not exceed the latent heat of condensation by more than 12 %; since other work suggests that the excess over the normal latent heat arises from the adsorption at relatively low pressures, there is probably a considerable range over which the adsorption is a function of the relative humidity and is independent of temperature.

Dr. W. Hirst (*Aldermaston*), **Mr. M. Griffith,** and **Miss E. M. Dresel** (*B.C.U.R.A., London*) (*communicated*): The theoretical paper of one of us (W.H.) originated from consideration of some experimental results obtained for the coal-methanol system. It is hoped to publish these results in due course, but as some of them bear on points raised in the Discussion it may be helpful to mention briefly two of our observations.

Example 3 of the theoretical paper suggests that when there is hysteresis the surface-energy lowering of a system may sometimes be calculated from the *desorption* isotherm. In our experiments we determined the methanol vapour sorption isotherms at two temperatures for a number of coals, and we also measured the heats of wetting by liquid methanol using a calorimetric method. The total energy changes were calculated from the adsorption and desorption curves by applying the Gibbs-Helmholtz equation to the free-energy lowering obtained on integrating the isotherm.* The calculated values were compared with the experimental heats of wetting. Owing to the nature of the apparatus the isotherm had to be extrapolated to saturation pressure but, for the adsorption curve, which is the important case here, this introduces no serious error into the calculated free-energy change. Allowance had also to be made for the difference

[37] *J. Inst. Elect. Eng.*, 1940, **86**, 369.

* See eqn. (1) of paper by Hirst.

between the free-energy lowering of the system when exposed to saturated vapour and when immersed in liquid. When the corrections were applied the heats obtained using the desorption curve agreed quite closely with the calorimetric heats, whereas those calculated from the adsorption curve were about 20% too low. The evidence therefore suggests that for this system the desorption curve provides the correct basis of calculation.

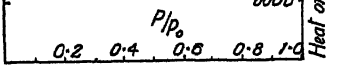
The differential heats of adsorption were also evaluated from the experimental isotherms. The net heats, i.e. the difference between the total energy of adsorption and the latent heat of condensation of liquid methanol (9,200 cal./mole), were found to vary over the course of the isotherm from about 3,500–4,000 cal./mole at low pressures to about 1,000 cal./mole at about 0·8 relative pressure. It is interesting to compare this variation with the variation predicted by the B.E.T. equation.

If the B.E.T. equation is written in the form

$$\frac{v}{v_m} = \frac{p/p_0\,.\,e^{\frac{E_1-E_L}{RT}}}{\left(1 - p/p_0\right)\left(1 - p/p_0 + p/p_0\,.\,e^{\frac{E_1-E_L}{RT}}\right)},$$

the heat of adsorption $RT^2\,.\,\mathrm{d}\log_e p/\mathrm{d}T$ is readily calculated. The result is

$$RT^2\,.\,\mathrm{d}\log_e p/\mathrm{d}T = \frac{E_1\left(2p_0 - p_0^2/p - p\right) + E_L\left(2p - 2p_0 - p\,.\,e^{\frac{E_1-E_L}{RT}}\right.}{p - p_0^2/p - p\,.\,e^{\frac{E_1-E_L}{RT}}}$$



This function is plotted on the diagram together with the experimental results for one of the coals. (The value for E_1 obtained experimentally was used to derive the points on the B.E.T. curve.) The lack of agreement is evident.

Dr. J. F. Duncan (*Harwell*) said: The so-called B.E.T. equation as it stands describes the shape of an adsorption isotherm only over ranges of p/p_0 from about 0·05 to 0·3. It has, however, been shown by Anderson[38] that the plot of p/p_0 against $\frac{p/p_0}{(1 - Kp/p_0)\,v}$ gives a straight line over ranges of p/p_0 from 0·05 to about 0·8, and that K has a value of 0·7 for nitrogen. This is in accordance with some unpublished results of mine using ethylene as an adsorbate, for which the Anderson constant K is 0·6–0·65. Anderson has shown that the necessity of including the constant K implies that the heat of sorption of the second to nth molecular layers is about 50 cal. less than the heat of vaporisation of the adsorbate. The fundamental assumption of the B.E.T. equation, namely, the equality of the heat of sorption of all except the very first molecular layer to the heat of vaporisation, is, therefore, not very far wrong.

The Anderson-modified B.E.T. equation is applicable for $0{\cdot}05 < p/p_0 < 0{\cdot}8$ which considerably overlaps the range of applicability of the Harkins equation $\log p = B - A/q^2$ in the range $0{\cdot}3 < p/p_0 < 0{\cdot}8$, when the B.E.T. constant c is greater than 50. For conditions under which they may be compared ($c > 50$) the two equations lead to the same surface area and are equally applicable.[39] We have, then, two equations of different mathematical form which describe nearly the same portions of the same isotherm. In principle, therefore, it should be possible to convert one into the other, or reduce them to a common mathematical form.

[38] Anderson, *J. Amer. Chem. Soc.*, 1946, **68**, 686.

[39] Harkins and Jura, *J. Amer. Chem. Soc.*, 1944, **66**, 1366.

I have been able to show (unpublished work) that

(1) if c is large, the Anderson-modified equation may be reduced to

$$\frac{p}{p_0} = \frac{1}{K}\left(1 - \frac{v_m}{v}\right) \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

for $0\cdot 3 < p/p_0 < 0\cdot 8$, where K is the Anderson constant, and v_m is the volume of adsorbate required to fill a monolayer; and

(2) the Harkins-Jura equation may be reduced to the form:

$$\frac{p}{p_0} = C\left(1 - \frac{v_m}{vD}\right) \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

$$\text{where } C = 2\cdot 303H + \tfrac{1}{2}, \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

$$D = (H + 0\cdot 217)F/H^{1/2}, \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

$$H = B + \log_{10}2, \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

$$F = \frac{3\cdot 69}{\sigma} \times k. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6)$$

σ = area occupied by 1 molecule on the surface (A.^{2})

(B is as defined in eqn. 11 of Dr. Foster's paper; v and v_m are measured in cc. N.T.P./g. adsorbent and Σ in m.^{2}/g.)

The mathematics in eqn. (2) involve two approximations introduced as a result of a logarithmic and a binomial expansion. It can be shown that provided $0\cdot 25 < p/p_0 < 0\cdot 75$ the error arising in eqn. (2) is always less than 5%; over the greater part of this range it is much smaller and can be neglected compared with experimental errors.

It will be seen that both equations reduce to the same form. By comparing eqn. (1) and (2), D might be expected to be unity, and the Anderson constant

$$K = \frac{1}{2\cdot 303(B + 0\cdot 3010) + \frac{1}{2}}.$$

Now by making a plot of $1/v$ against p/p_0, a curve such as Fig. 1 is obtained. Assuming that this obeys the equation

$$p/p_0 = \frac{1}{K}\left(1 - \frac{v_m}{vD}\right) \quad . \quad . \quad . \quad . \quad . \qquad (7)$$

the middle, straight portion is produced to each axis, from which it will be seen that

(1) the reciprocal of the intercept on the $1/v$ axis equals $\frac{v_m}{D}$.

(2) the intercept C on the p/p_0 axis is equal to the reciprocal of Anderson constant K.

An experimental test of this equation has been made, using the isotherms given by Harkins and Jura, and also Brunauer, Emmett and Teller. Using seven nitrogen isotherms, the following values have been obtained for the different quantities mentioned:

$D = 0\cdot 89 \pm 0\cdot 08$; Anderson constant $K = 0\cdot 70 \pm 0\cdot 07$
Harkins constant $B = 0\cdot 39 \pm 0\cdot 03$; $F = 0\cdot 91 \pm 0\cdot 05$
Harkins constant $k = 4\cdot 01 \pm 0\cdot 25$ (value given by Harkins 4·06).

Similar results have also been obtained using ethylene as adsorbate (unpublished work).

It will be noticed that the quantity D is not quite unity, as predicted by eqn. (1), although this is not at variance with eqn. (2). The quantity F is also seen to be very close to unity for nitrogen, and this was also found for ethylene. Assuming F to be unity whenever c is large and the above equation is valid, we can use (6) to obtain a rough value of the Harkins constant k from a given value for the area occupied by the adsorbate. Thus, if we assume Emmett's value of 14·8, 56·6 and 64A.^{2} for water, n-butane, and n-heptane, we get Harkins' k to be 4·02, 15·3 and 17·4 respectively. The corresponding values given by Harkins are 3·69, 13·6 and 16·9. It will be seen, therefore, that to a first approximation, *F* must also be unity for these adsorbates and that the assumption of a given value of *k* is tantamount to an assumption of a value for the area occupied by one adsorbate molecule.

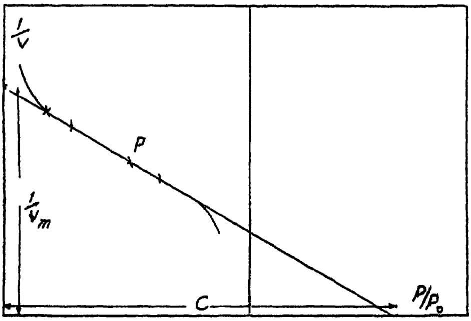


FIG. 1.

A further use of eqn. (7) is that it now makes possible the approximate determination of the surface area of a solid from a single point on the isotherm which is in the range $0{\cdot}3 < p/p_0 < 0{\cdot}7$. If the Anderson constant *K* is known, this gives us the intercept *C* on the p/p_0 axis (Fig. 1). If a single point on the isotherm is taken at *P*, v_m may be determined by joining *C* to *P* and producing to the $1/v$ axis. The merits of this method will be discussed later, but it is estimated that it will give about 20% accuracy.

Dr. S. M. Neale (*Manchester*) said: The assumption in Schofield and Talibuddin's paper that the negative charge on cellulose was wholly due to dissociation of carboxylic acid groups, and that consequently it would be wholly or mainly suppressed at *p*H 1·3, was not in accord with experiment. Cotton cellulose almost entirely free from COOH groups showed a strong negative potential against aqueous solutions and the introduction of carboxylic acid groups by alkaline oxidation had relatively little effect.

The great majority of neutral substances which were free from ionising groups, showed a negative charge in contact with water. The negative charge on cellulose could be neutralised only by the adsorption of cations with a strong specific affinity for the fibre, such as Al^{+++} or Th^{++++} or the cations of the basic dye Victoria Blue B. These statements, though originally based on measurements of *zeta* potential,[40] had recently been confirmed by an entirely independent method, by means of which the Donnan potential between fibre and solution could be measured.

Dr. R. K. Schofield (*Harpenden*) said: In reply to Dr. S. M. Neale, I do not know of any reliable experiments that prove the presence, at low *p*H values, of negative charges on cotton cellulose other than those due to the very small fraction of the few carboxyl groups dissociated to $-COO^-$ groups. Measurements of electrophoresis are not very serviceable, because the measured velocities are by no means proportional to the surface charge density. From the description Dr. Neale has given me of his recent experiments, I conclude that he has measured diffusion potentials which are not directly related to the amount of negative charges on the cellulose.

I am confident that when cotton that has suffered no oxidation is examined by our method, the results will show that the charge at *p*H 1·3 is too small to be measured. The charge, *E*, per 100 g. of fibre at *p*H 6 can be formed by measuring exchangeable calcium. If this charge remained undiminished with fall in *p*H to 1·3, then $v_{1\cdot3}$ would be found to be as great as v_6. If, in fact, $v_{1\cdot3}$ is less than v_6 we can obtain the limit *V* of the difference v_B for very low values of the concentrations, n_1. For untreated cotton *E* is less than for white jute, so we may expect Donnan's equation to be applicable. If the charge at *p*H 1·3 is indeed negligible then we should have from eqn. (2) of our paper:

$$\frac{E}{nV} = \left(1 - \frac{v_B}{V}\right)^{-1} - \left(1 - \frac{v_B}{V}\right)$$

If, however, the right-hand side of this equation were found to be consistently only a fraction of $\frac{E}{nV}$, this would show that in going from *p*H 6 to *p*H 1·3, the charge *E* had only diminished by this fraction.

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[40] Neale and Peters, *Trans. Faraday Soc.*, 1946, **42**, 478.

I doubt whether in practice we ever deal with a "neutral" or "inert" surface, unless by a "neutral" surface we just mean one that, under particular conditions, carries no charge, and so gives rise to no diffuse double-layer.

Dr. R. M. Barrer (*London*) said: I have in my paper presented some old and some new aspects of the kinetics of flow in capillaries and porous media. In so doing, a brief quantitative inspection of transient and steady states of flow has been given for a number of well-recognised types of fluid transport, any one of which may be shown by water. Special attention has been given to transition regions between one such type and another, for here formulation has sometimes been incomplete. Transition regions considered include:

(1) penetration under the combined influence of pressure head and surface tension,

(2) overlapping of streamline flow and molecular streaming, and

(3) merging of molecular streaming with surface diffusion—a hitherto neglected feature.

From an understanding of transition region (2), Ridgen has amended the Kozeny method for gases to give more accurate information as to the *geometrical* internal surface of porous solids. The Kozeny method is much used for this purpose using incompressible fluids, and has been discussed in several aspects by Carman (this Discussion). It was therefore not reviewed by me.

However, I have developed and drawn attention to a second method of obtaining similar information as to *geometrical* internal surface—the Adzumi method, depending wholly upon overlap of streamline flow and molecular streaming. This method does not seem to have received much attention previously, but is certainly worth consideration.

Finally, I have given all the necessary quantitative data for a third method of deriving a mean radius, and number of pores per unit cross-section of the porous bed. This method depends on measuring the time lag L given by eqn. (32), and also the steady state permeation rate, P, given by

$$P = \frac{AN8/3 . \pi r^3}{\sqrt{2\pi mkT}} . \frac{(p_1 - p_2)}{l},$$

where A is the cross-section of the bed and N the number of pores per unit area. The value of r is derived from the expression for L, and substitution in the above relation then permits N to be determined. The limitations in so determining r, N, and thus a geometrical internal surface are similar to those in the Kozeny and Adzumi methods.

These three methods might make an interesting complementary study referring as they do to incompressible liquids, or to gases (Kozeny), to gases in the overlapping region of Poiseuille and Knudsen flow (Adzumi), and to gases in the Knudsen flow range (Barrer).

Finally, I wish to draw attention to the transition region between molecular streaming and surface diffusion. The treatment given provides, in principle, a method of studying both adsorption and surface diffusion. If one works with capillaries of known decreasing radii, or with columns of a porous material of uniform particle sizes, one may measure the time lag L as a function of $1/r$. In the absence of surface effects, a linear relation exists between L and $1/r$ according to eqn. (32). When a proportion of the molecules is immobilised by adsorption the curve of L against $1/r$ will bend increasingly *away* from the axis of $1/r$ as $1/r$ increases. Here $L = \frac{l^2}{6D}$, and D is given by eqn. (33). Finally, if there is a considerable surface diffusion of adsorbed molecules the curve of L against $1/r$ will bend increasingly *toward* the axis of $1/r$ as $1/r$ increases, D being now given by eqn. (35).

Thus there are several fields interesting in the study of surface chemistry, but so far largely neglected, which can be investigated by quite simple kinetic experiments involving molecular streaming through single capillaries or through porous media.

Dr. R. I. Razouk (*Cairo*) (*communicated*): A special case of flow of liquids in porous media which is of value in calculating equivalent radii, tortuosity factors and contact angles is the rise of liquids in vertical capillary tubes or porous beds under the effect of their surface tensions only. When a capillary tube is brought into contact with a liquid, the latter will rise in it until surface tension forces are equalised by gravity forces, and the rate of rise of liquid will be given by Dr. Barrer's eqn. (3) in the form :

$$\pi r^2 \frac{dx}{dt} = \frac{-\pi r^4 g d x + 2\pi r^3 \sigma \cos\theta}{8\eta x} . \qquad (a)$$

The density and viscosity of the vapour are neglected in comparison with those of the liquid. It follows that :

$$x \frac{dx}{dt} = \frac{r\,\sigma \cos\theta}{4\eta} - \frac{r^2 g\, d\, x}{8\eta} . \qquad (b)$$

On integration,

$$-\beta\, t = x + \frac{\alpha}{\beta} \ln\left(1 - \frac{\beta}{\alpha} x\right), \qquad (c)$$

where $\alpha = r\,\sigma \cos\theta/4\eta$, and $\beta = r^2 g\, d/8\eta$.
A more general form of eqn. (*c*) was first given by Washburn in 1921.[41]

This equation shows that the maximum height of a liquid in a capillary tube is reached after infinite time and is given by :

$$x_0 = \alpha/\beta = \frac{2\ \sigma \cos\theta}{r\,.\,g\,.\,d}.$$

For small values of x, i.e. in the early stages when the effect of gravity is negligible, eqn. (*c*) gives on approximating the expansion of the logarithmic term,

$$x^2/t = 2\alpha = r\sigma \cos\theta/2\eta,$$

which is the well-known equation of Washburn [41] and Rideal [42] for the flow of liquids in horizontal tubes.

The two constants of eqn. (*c*) can be determined from experiments on rates of capillary rise and cos θ and r will then be given by

$$\cos\theta = \sqrt{2\,\frac{\alpha^2 g\, d\, \eta}{\beta\, \sigma^2}},$$

$$r = \sqrt{\frac{8\,\eta\,\beta}{g d}}\ .$$

When the capillary possesses a tortuosity factor k, Dr. Barrer's eqn. (6) gives on integration for the special case under consideration :

$$-\frac{\beta}{k} t = x + \frac{\alpha}{\beta k} \ln\left(1 - \frac{\beta}{\alpha} k x\right) \qquad (d)$$

which reduces for small values of x to Eley and Pepper's eqn.[43]

$$x^2/t = r\sigma \cos\theta/2\eta k^2$$

Eqn. (*d*) contains two constants which are functions of r, k and cos θ, so that if any of these is known, the remaining two can be evaluated from rate measurements.

This equation has been found to fit satisfactorily the results of experiments on the rate of capillary rise of liquids in the pores of charcoal already saturated with their vapours.[44]

Rectangular prisms of charcoal were suspended from a spring balance of the McBain-Bakr type so that their axes of conducting pores were vertical. After outgassing the charcoal at 300° c., it was exposed to the saturated vapour of the liquid and when equilibrium was attained the liquid was brought into contact with the charcoal. The distance through which the liquid penetrated the charcoal was evaluated from the gain in weight and a knowledge of the pore volume of the charcoal.[45]

[41] Washburn, *Physic. Rev.*, 1921, **17**, 276.
[42] Rideal, *Phil. Mag.*, 1922, **44**, 1154.
[43] Eley and Pepper, *Trans. Faraday Soc.*, 1946, **42**, 697.
[44] Razouk, *Ph.D. Thesis* (Cairo University, 1939).
[45] For details, see Bangham and Razouk, *Trans. Faraday Soc.*, 1937, **33**, 1463.

As an example, Fig. 1 shows the rate of capillary rise of ethyl alcohol and benzene at 28° C. in the same prism of charcoal. The circles represent the experimental points of two runs in each case and the full lines represent the equations:

$$0{\cdot}0060\ t = x + 13{\cdot}0 \ln\left(1 - \frac{x}{13{\cdot}0}\right)$$

$$0{\cdot}0128\ t = x + 14{\cdot}8 \ln\left(1 - \frac{x}{14{\cdot}8}\right)$$

for ethyl alcohol and benzene respectively.

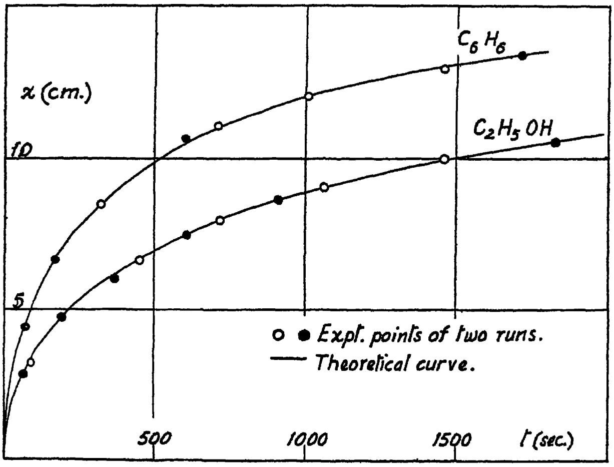

FIG. 1.—Rate of penetration of benzene and ethyl alcohol in charcoal.

The contact angle of ethyl alcohol and benzene on charcoal is probably very small. Taking $\theta = 0$, the equivalent radius and tortuosity factor of the charcoal can be calculated from the constants of the above equations, and the values obtained are shown in the adjoining table.

CAPILLARY CONSTANTS OF CHARCOAL

Liquid	r (cm.)	k
Ethyl alcohol ..	$1{\cdot}42 \times 10^{-3}$	3·11
Benzene	$1{\cdot}45 \times 10^{-3}$	3·05

The agreement is excellent, especially if it is remembered that in eqn. (*a*) and Dr. Barrer's eqn. (3) and (6), the inertial effects and kinetic energy of flow were neglected. If the latter effect is taken into consideration the differential equation for the rise of liquids in vertical tubes becomes:

$$\frac{d^2x}{dt^2} + \frac{8\eta dx}{r^2 x dt} + g = \frac{2\sigma \cos\theta}{rx}, \qquad (f)$$

which unfortunately does not give a simple solution.

Mr. D. I. W. Atkinson (*London*) said: The paper by Dr. R. M. Barrer contained some equations for the rate at which one liquid would be displaced by another in a capillary tube. However, a bed of solid particles did not behave precisely as a large number of capillaries, and a liquid was, in general, not completely displaced from such a bed. He considered that, in practice, one was more concerned with the extent to which the displacement was complete, rather than the rate at which it took place under a given driving force, and explained that he had carried out some experimental work designed to show which factors were most important in determining the amount of a liquid that could be displaced.

Some work had been carried out initially using steel spheres to form the solid bed. It was possible to displace the bulk of an organic liquid from the bed with water, but there was invariably a little of the organic liquid left behind in the form of a lens-shaped ring around each point of contact of the spheres. The size of the rings was substantially constant throughout the bed, but varied with the system of liquids used. Fig. 1 shows part of a bed of steel spheres, ¼ in. diam., which was, at first, saturated with heptane. Water was then moved gradually upwards through the bed and the heptane residue formed the rings at the points of contact, surrounded by water. Fig. 2 shows the system, liquid paraffin-water, and it was observed that the heptane rings were smaller than the liquid paraffin rings, showing that the displacement of the heptane was more complete. It was possible, having measured the average size of a ring and knowing the mathematical expression for its volume, to calculate the percentage displacement which would be obtained for a given mode of packing, i.e. for a given number of points of contact. This value agreed well with the actual volume displaced in the experiment. This volume did not seem to be dependent upon the interfacial tension between the two liquids concerned, but appeared to be inversely proportional to the viscosity of the liquid displaced ; thus, the greater the viscosity, the less the amount displaced.

Viscosity, however, could not be the only factor concerned, for, if the bed were formed of glass spheres or sand and fine gravel, the amount displaced was greater than that obtained for the same liquids, when steel spheres were used, and was almost independent of the system of liquids.

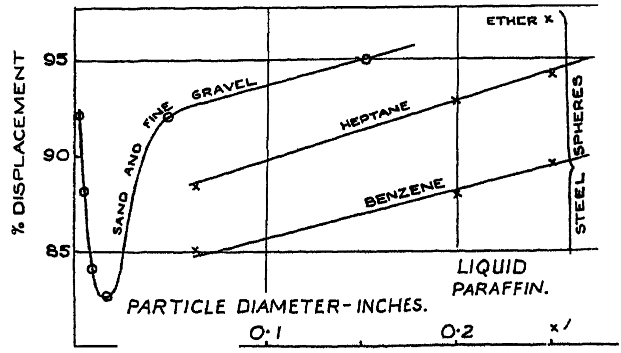

Fig. 3.

Fig. 3 shows the results in relation to one another. The curve for sand and fine gravel represented the average results obtained, using the systems benzene, heptane and ether displaced by water and ethyl acetate by a saturated solution of itself in water. In the coarse size region, the gravel and steel spheres showed a similar tendency to increased displacement with increased particle size. The displacement would be expected to approach 100%, if spheres of very large size were employed. The sand curve showed a minimum at a particle size of 1/100 in., and the displacement thereafter increased with decreasing particle size, due, it was thought, to capillary forces being dominant in this region.

It had been shown from measurements of interfacial contact angles that the organic liquids used wet steel preferentially to water, but wet glass less than water, and it was proposed that that was the reason why higher displacements were obtained using glass and sand rather than steel particles.

To summarise, it seemed that if the displacing liquid wetted the solid preferentially to the displaced liquid and both were of low viscosity, the amount displaced was independent of the liquids used and was dependent only on particle size and type of packing. If the liquid displaced wetted the solid preferentially to the displacing liquid, the amount was less and was dependent on the viscosity of the liquid displaced.

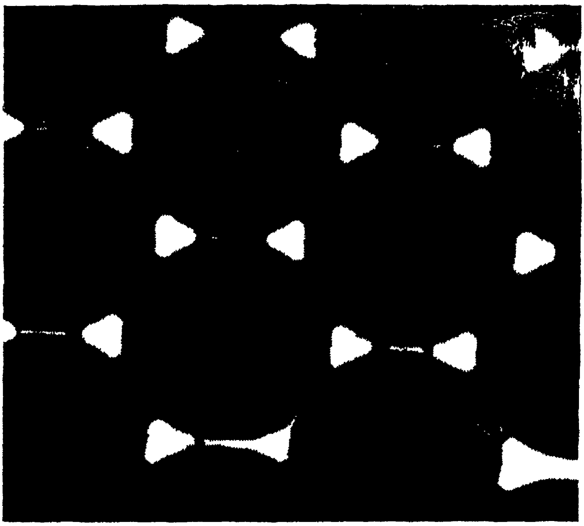

FIG 1.—Heptane displaced by water from a bed of steel spheres.

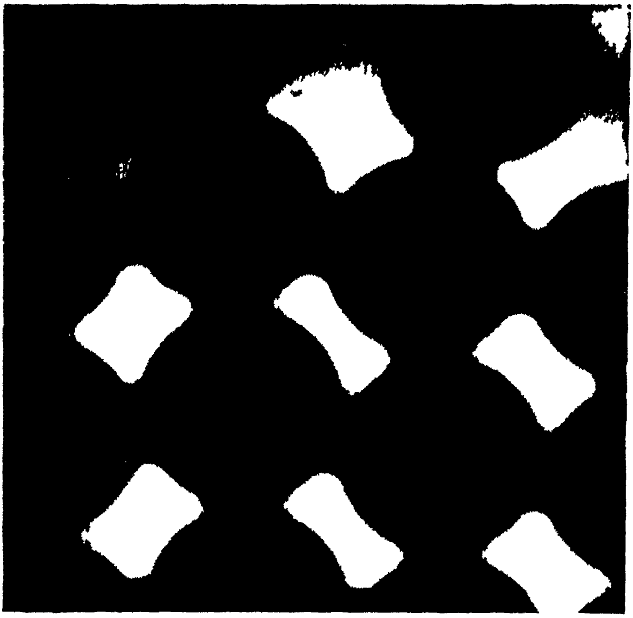

FIG 2.—Liquid paraffin displaced by water from a bed of steel spheres.

Mr. C. N. Davies (*London*) (*communicated*) : Consider two solid spheres of radius a which touch at T. Around T is a ring of liquid having the meniscus MM′ within which the pressure is P_1 and outside which the pressure is P_2. The angle of contact, AMB, is equal to θ and angle TOM is φ. Let MX $= x$, TD $= R$ and CD $= r$.

If gravitational effects are negligible in comparison with capillary forces, P_1 will be constant at all points inside the meniscus and r and R will be the radii of circles. On the other hand, if gravity is appreciable, the orientation of the spheres would have to be considered and the intrinsic equation for the meniscus deduced. Taking the former condition as a first approximation we have

$$\frac{P_2 - P_1}{\sigma} = \left(\frac{1}{r} - \frac{1}{R}\right)$$

where σ is the surface tension.

From the geometry of the figure it can be shown by substituting for r and R that

$$\frac{x(P_2 - P_1)}{\sigma} = \cos(\theta + \varphi)\left\{\frac{\cos\theta\sin\varphi - (1 - \cos\varphi)(2 + \sin\theta)}{\cos\theta\sin\varphi - (1 - \cos\varphi)(1 + \sin\theta)}\right\} \quad . \quad (1)$$

For the liquid to be stable it is necessary that P_2 should be greater than P_1. If the quantity of liquid is increased $(P_2 - P_1)$ diminishes and, if (1) remained valid, would equal zero when

$$\frac{\cos\theta}{2 + \sin\theta} = \tan\frac{\varphi_{\max}}{2} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

which would therefore relate $\varphi_{\max}$, from which the maximum volume of retained liquid could be calculated, to the angle of contact, θ.

The following table shows the relation between these quantities :

Angle of contact	$\varphi_{\max}$ Eqn. (2)
0°	53°8′
20°	43°44′
40°	32°20′
60°	19°48′
80°	6°40′
90°	0

It is evident, however, when P_2 is only slightly greater than P_1 that gravitational forces must become important because capillary effects are then almost zero. A solution allowing for the gravity effects is really required for this condition and would involve the intrinsic equation of the meniscus. However, in practice, values of $\varphi_{\max}$ as large as those given in the table would not be attained on account of dynamic factors. The residual liquid would also depend on the density and viscosity. Perhaps if the surrounding medium, P_2, had a density only slightly different from that of the residual liquid, P_1, it might be possible to approach more closely to the theoretical values of $\varphi_{\max}$ given above. It should be noted that (2) is independent of the interfacial tension and of the radius of the spheres. Experience with the process of drop separation, which presents some analogies, suggests that in the dynamic problem the quantity of residual liquid could be expressed as a function of $\frac{\rho a^2 g}{\sigma}$, ρ being the effective density and g the acceleration due to gravity. Possibly the angle of contact could be allowed for in a study of various liquids by expressing the difference between the observed values of $\varphi_{\max}$ and those given by (2) as a function of this dimensionless group.

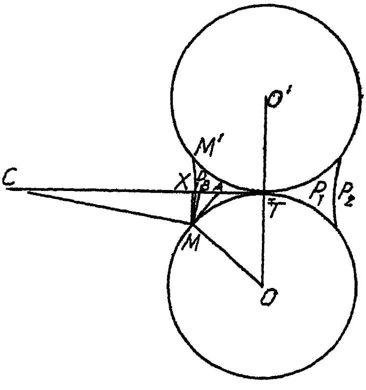

FIG. 1.—Drainage from beds of small equal spheres.

Mr. D. I. W. Atkinson (*London*) (*communicated*) : I was very interested in the communication of Mr. Davies, giving his theory of the drainage of liquids from porous beds. After making the assumption that there is no pressure differential across the liquid surface, his geometrical analysis of the problem is undoubtedly correct, but when the results to which it leads are considered it is found that the assumption is invalid.

In the first place, rings of liquid, having a zero angle of contact with a solid, could not exist with an angle φ of 53° 8′, in a bed of particles. In Fig. 1 and 2, it is shown that, for spheres in tightest or rhombohedral packing, the maximum possible value of φ is 30°, and, for open cubical packing, the maximum value is 45°.

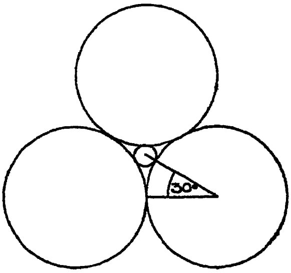

FIG. 1.

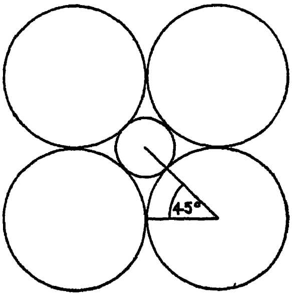

FIG. 2.

Some experiments I have carried out show that φ, in practice, is about 25°, or a residue of 7 % by volume is left in a bed of 40 % voids. The same result is obtained for all liquids having a zero contact angle with the solid and is independent of density, surface tension and viscosity, provided sufficient time is allowed.

The explanation is presumably that suggested by Haines,[46] that a pressure of $\frac{12{\cdot}9T}{r}$ is required to force an air bubble through the narrowest constriction of a bed in closest packing and $\frac{4{\cdot}8T}{r}$ for open packing, and that the pressure deficiency, under the liquid rings, would have a similar value ; T is the surface tension of the liquid and r is the radius of the spheres. A value of φ of 25° corresponds to a pressure deficiency of $\frac{7{\cdot}5T}{r}$ which is a very reasonable figure for a bed consisting of 40 % voids, or approximately mid-way between close and open packing.

Dr. A. Klinkenberg (*The Hague*) said : Referring to Mr. Atkinson's contribution to the Discussion, I should like to mention that I have recently prepared a paper in which the importance of contact angles on displacement was also observed. Water was found to displace non-polar liquids, such as *iso*-octane or benzene, to a much greater extent from a column of sand than it does from oleophilic solids like sulphur, of similar grain size. Evidently here the contact angle is the determining factor. Also, displacement of water from sulphur by benzene is more complete than displacement of benzene from sulphur by water. Here again the contact angle seems the only possible cause of the difference.

As regards the influence of the viscosities of the liquids, I hold the opinion that the ratio of the viscosities is important. If the displacing liquid has a higher viscosity than the displaced liquid, any accidental disturbances of the moving boundary will tend to be corrected automatically. Along any streamline where the boundary has advanced too far, the resistance will be higher and thus the flow retarded. Inversely, if the boundary has lagged behind, it will move faster. If, however, the displacing liquid has the lower viscosity, these disturbances will tend to aggravate, resulting in by-passing of the viscous liquid by the less viscous one. Some experiments have shown that displacement of octane and kerosene from sand by water is practically complete. More viscous mineral oil fractions, however, are by-passed to a considerable extent by the water.

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[46] Haines, *J. Agric. Sci.*, 1927, **17**, 264.

Mr. J. F. Pearse (*London*) said: At Imperial College we are studying the air drying of solids and the manner in which moisture escapes from a solid during drying. If a solid be dried from the top surface only, in air of constant temperature, humidity and velocity, then the plot of drying rate against moisture content is shown in Fig. 1. AC is called the constant rate period, ending at the critical point, C, and CD the falling rate period. It has been shown that, in the constant rate period, all evaporation occurs at the surface and it behaves as though completely wet. The water must move to the surface by some mechanism and, in granular solids, it is by capillary movement.

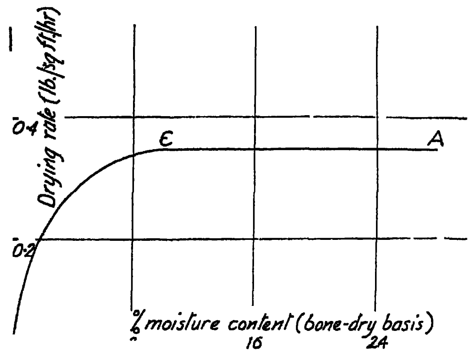

FIG. 1.—Drying rate curve.

From Haines' theory, it can be shown that if a solid consisting of uniform spheres in uniform packing be dried, there will be no constant rate period, for the funicular state cannot extend to the surface. Thus, the existence of a constant rate period must depend on the heterogeneous nature of the pore space in a solid, and the moisture moves to the surface from larger pores within the body, by way of interconnected fine-pore spaces. It must be assumed that there are sufficient fine pores at the surface to be equivalent to a completely wetted surface.

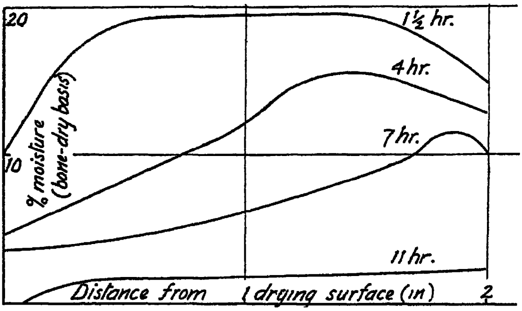

FIG. 2.—Moisture distribution curves. Glass spheres (135μ av. diam.).

Assuming there is no resistance to capillary flow of moisture, the amount of moisture that could be evaporated during the constant rate period and moisture distribution curves in solids during drying could be derived from a knowledge of pore size distribution.

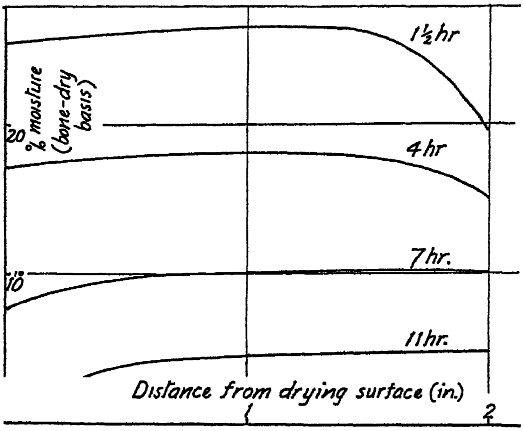

FIG. 3.—Moisture distribution curves. Silica sand (45μ av. particle size).

Moisture distribution studies have been carried out with solids, consisting of glass spheres (135μ diam.), silica sand (average particle size, 45μ) and silica sand (average particle size, 15μ), respectively. Fig. 2 shows curves obtained with a solid of glass spheres, dried at high drying rate and at drying times of 1½, 4, 7 and 11 hr. respectively from an initially saturated condition. The curves show a combination of capillary and gravity effects, the decrease in moisture content at the bottom of the solid being due to the very open pack-

Similar curves with a solid consisting of silica sand of average particle size 45μ, are shown in Fig. 3. Here capillary effects far outweigh gravity effects and so the distribution of moisture is almost uniform, except for the effect as noted above.

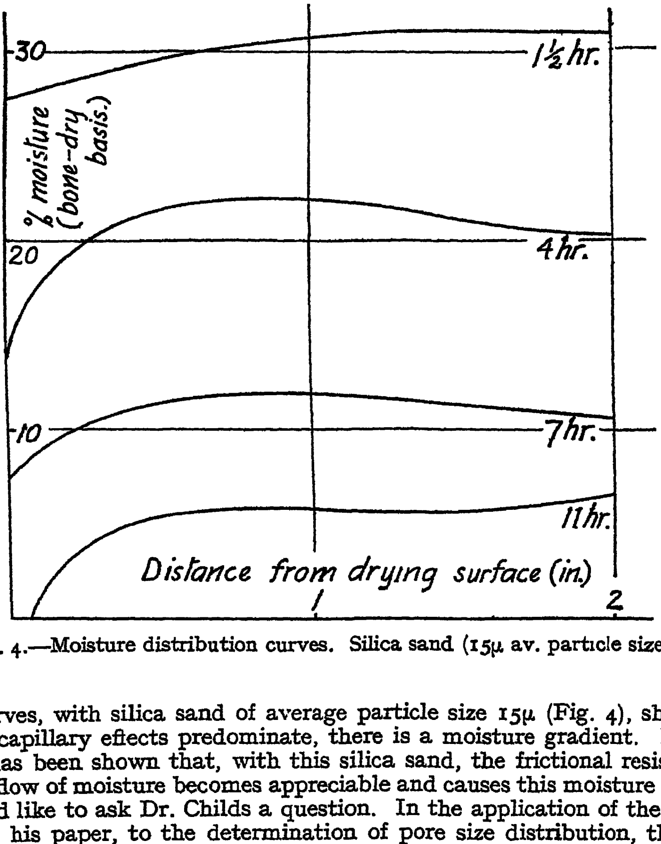

FIG. 4.—Moisture distribution curves. Silica sand (15μ av. particle size).

The curves, with silica sand of average particle size 15μ (Fig. 4), show that, although capillary effects predominate, there is a moisture gradient. By other tests, it has been shown that, with this silica sand, the frictional resistance to capillary flow of moisture becomes appreciable and causes this moisture gradient.

I should like to ask Dr. Childs a question. In the application of the curve of Fig. 2, in his paper, to the determination of pore size distribution, the actual pore sizes are calculated from the equation for rise of water in a capillary tube. On the other hand, Haines, with solids of uniform spherical particles, considers the sizes of the waists connecting the pore spaces. Is the former treatment only suitable for solids consisting of angular particles and how accurate is it ?

Dr. H. C. Brinkman (*Holland*) said : A theoretical derivation may be given of a formula, which is analogous to the Kozeny-Carman formula, for the rate of flow through beds or swarms of spherical particles.

The rate of flow through the bed of particles is represented by an equation which describes the equilibrium between the pressure gradient, the viscous stresses and the damping force caused by the particles [47] :

$$\operatorname{grad} p - \eta \Delta v + \frac{\eta}{k} v = 0, \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

where k is the permeability of the bed, η the viscosity of the fluid, p the pressure and v the rate of flow. The nice point is, that this equation approximates Darcy's equation

$$v = -\frac{k}{\eta} \operatorname{grad} p$$

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[47] Brinkman, *Appl. Sci. Res. A*, 1947, 1, 27.

for low values of k and the Navier-Stokes equation of hydrodynamics

$$\operatorname{grad} p - \eta \Delta v = 0$$

for high values of k.

Now the value of k in eqn. (1) is calculated in the following way. The force exerted on one particle of the bed is found by calculating the flow round this particle in detail while the influence of the other particles is represented by the term $\frac{\eta}{k} v$ in the equation of flow. By multiplying this force by the total number of particles, the total viscous force on the bed is obtained. This leads to an implicit equation for the permeability k, which yields

$$k = \frac{\rho^2}{18}\left[3 + \frac{4}{1-\varepsilon} - 3\left(\frac{8}{1-\varepsilon} - 3\right)^{1/2}\right] \quad . \quad . \quad (2)$$

where ρ is the radius of a particle and ε the porosity of the bed.

For the rate of flow through the bed we obtain

$$\frac{6\pi\eta\rho N u}{\Delta p/L} = V\left[1 + \frac{3(1-\varepsilon)}{4}\left(1 - \sqrt{\frac{8}{1-\varepsilon} - 3}\right)\right] \quad . \quad (3)$$

where u is the rate of flow, N the number of particles, L the length and V the volume of the bed. This relation coincides numerically with the Kozeny-Carman relation in the porosity interval 0·8 — 0·4. For porosities nearing the value of 1 it leads to the Stokes formula for the viscous force on isolated particles. For low values of the porosities the model has to be refined.[48]

Mr. C. N. Davies (*London*) said: I have been collecting data on the flow through fibrous media in connection with the study of air filters. These are of interest because an unusually wide range of porosities is covered. Dimensional considerations lead to the formula

$$\frac{RAd^2}{\eta Q t} = \rho = \mathrm{f}(c),$$

where R = resistance, A = cross-sectional area and t = thickness of the filter; Q = flow through it, η = viscosity of the fluid, d = diam. fibres, and c = the fraction of available space occupied by the fibres = $(1 - \varepsilon)$, where ε is the porosity. The function f must depend on the shape of the fibres and their packing qualities. It is not appreciably dependent on length.

If we assume the fibres to be cylindrical and that the Kozeny-Carman law applies (with constant = 0·18) we obtain

$$\mathrm{f}(c) = \frac{89c^2}{1 - c^3}.$$

Actually the data for a wide variety of types of fibre over a range of c from 0·006 to 0·3 are spread over a fairly narrow band about the curve

$$\rho = 64c^{1\cdot5}(1 + 56c^3).$$

A unique curve would result if all types of fibre were geometrically similar and packed in the same way. The fibres in filter pads tend to lie mainly across the flow owing to the nature of the fibres and the method of construction; this is one reason for the small scatter observed about the empirical expression above. The special experiments of Sullivan and Hertel with fibres parallel to the flow give a much lower resistance.

Hence, the Kozeny-Carman equation breaks down for fibrous media and predicts too low a resistance for normal types of bed. The error is greatest for high porosities; for values of c between 0·2 and 0·3 the error is quite small.

Prof. E. Ernst (*Pécs, Hungary*) (*communicated*): As already described elsewhere (1938), I deduced theoretically and verified experimentally the phenomenon of thermo-osmosis. The basic train of thought is as follows: by dissolving, e.g. sugar in water, the vapour pressure of the latter decreases. This can be compensated by rising temperature, because the higher the temperature the greater is the vapour pressure. In the equation

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[48] Brinkman, *Appl. Sci. Res.* (to appear shortly).

$$\Delta T = \frac{RT^2 \ln \frac{p_0}{p}}{H + \frac{n_1 h}{n_0} - RT \ln \frac{p_0}{p_1}},$$

derived from the law of Clausius-Clapeyron, ΔT shows the rise of temperature needed for compensating the decrease of vapour pressure from p_0 to p_1 caused by dissolution, and H is the heat of evaporation.

In the wall of a clay-cylinder a solution of egg albumin was introduced by suction; the cylinder was dried and put in a wider cylinder of glass, both being afterwards filled with the same solution of $K_4Fe(CN)_6$. The solution inside the clay-cylinder was heated by an electric current through an insulated roll of constantan wire, and the solution outside was cooled by putting the whole system in a refrigerator. After 3 weeks, the solution inside had diminished and that outside increased by 18 cc., the variation in concentration inside and outside being measured by titration with $KMnO_4$.

Dr. G. S. Hartley (*Harston*) said: It was probably not the intention of Hutchison, Nixon and Denbigh to imply, by their careful negation of thermal osmosis in one particular system, that the phenomenon may not be real in other cases also and not in some cases perhaps of considerable importance. The phenomenon begins with the Soret effect in simple liquid solutions. In general, if a temperature gradient is maintained (without convection) in a solution, a gradient of composition is induced. It is important to appreciate that there is in this case no membrane artificially restraining equilibrium in one species. Both presumably are driven towards the colder region but, in the condensed phase, no appreciable movement is permissible. Movement of one component with respect to the other can occur, and is measurable, depending on the relative driving forces. The effect is thus a second-order molecular force effect and as such highly specific. No theory can yet predict in which direction even, let alone to what extent, change of composition in any system will occur. The majority of recorded measurements are for salts in water. Here the salt increased the density of water and therefore, were it to migrate towards the warmer (upper) region, convective instability would neutralise the migration. Thus it appears that salts move towards the cold (to varying extents) or do not move at all. In most cases the zero values are probably would-be negative values.

Debye had reported large thermal diffusion effects in polymer solutions and Toms and the speaker had also demonstrated this. The latter preferred to call the process thermal "migration," as a real relative movement of the components of the solution was involved. Since the forces operating would be expected to increase with molecular size and more rapidly than the resistance coefficient, it was to be expected, and was found, that thermal migration proceeded to a greater extent in polymer solutions than in simple solutions and at least as rapidly. Here it was of interest to note that the high viscosity of the solutions so stabilised the system against convection that movement of a heavier-than-solvent polymer to the hot region could be demonstrated.

Since the effect increased with molecular size it was entirely to be expected that, could the large molecules increase still further and become fixed as the matrix of a porous structure, the porous system would show thermal osmosis in marked degree. The magnitude, however, and even the direction, of the process could not be predictable from any other known properties. The speaker thought that a curious and striking phenomenon very evident on disturbed chalk downland in frosty weather, might be a naturally occurring case of thermal osmosis in a porous material. Lumps of chalk lying on the ground would be found to have a quite thick layer of ice on their upper surface. The ice was glassy, not hoary, and did not form on a lump of chalk suspended just above the ground. The water did not therefore come from the air but from the ground and presumably through the chalk. He had even seen "stalagmites" of glassy ice some 4 in. high erected from turf and found on excavation to arise from lumps of lightly buried chalk. Water flow induced by a thermal gradient seemed the most probable cause and would account for the specific occurrence on a particular porous material.

Dr. K. G. Denbigh (*Welwyn*) (*communicated*) : In reply to Dr. Hartley, perhaps he had not made it sufficiently clear that he regarded the absence of any measurable thermo-osmosis of water across a sintered glass disc as being due to the heat effect, Q^*, of eqn. (12) as being negligibly small in this particular system. He agreed with Dr. Hartley about the generality of the phenomenon and, in fact, the derivation of eqn. (12) did not depend on any specific properties. The magnitude of the thermo-osmotic effect in any particular system depends on the value of Q^*. The molecular significance of this quantity is still by no means clear.

It seemed that eqn. (12) could also be obtained by a method alternative to that used in the paper. Here the membrane itself was considered as the thermodynamic system under discussion and it was regarded as the seat of a Soret effect between the molecules of the diffusing substance and the immobile molecules of the membrane. This was probably the link between Dr. Hartley's views of the phenomenon and his own.

An interesting example of thermo-osmosis which was being studied was that of CO_2 through a thin membrane of rubber. The rubber is permeable to the gas by a process of solution, and if the two sides of the membrane are maintained at different temperatures the gas passes through from the cold to the warm side at a steady rate. By using a closed gas circuit containing a bubbler, it was possible to demonstrate a circulation of gas round the system. This circulation seems to continue indefinitely. The efficiency of the system as a heat engine is very low. The pressure difference which is necessary to prevent circulation is quite appreciable and amounts to a few cm. Hg when the temperature difference is of the order of 10–20° c.

Dr. R. K. Schofield (*Harpenden*) (*communicated*) : There is some confusion regarding the meaning of φ in eqn. (1) in Child and George's paper. In the sentence that follows we are told that, at a given height, the equilibrium value of P will vary with p and π, so that $(P - p - \pi)$ is constant. This is only true for the state of complete equilibrium reached when the ionic activities have also become equal, e.g. by diffusion. A manometric measurement, as in the pressure-plate method of Richards, is not sufficient to give φ as defined in eqn. (1). It can, however, be obtained from a sufficiently accurate measurement of relative vapour pressure in certain circumstances from the freezing-point depression.

It is not correct to say that φ determines the moisture content of a given soil ; it is the " suction " which, apart from hysteresis, does this. The component of φ due to free solutes as distinguished from ions held in the Göuy layers makes no direct contribution to the " suction."

Manometric methods using suitable membranes give the " suction " directly. To get the " suction " from the vapour-pressure or freezing-point depressions, we must subtract from the total reduction of free energy of the water the part due to free solutes.

Dr. E. C. Childs (*Cambridge*) said : Pore geometry is complicated even for such an idealised medium as a set of uniform spheres in close packing, and precise interpretation of a moisture characteristic is impracticable. It is true that the moisture characteristic for decreasing moisture content indicates rather the size-distribution of the necks, whilst that for increasing moisture content may be interpreted as indicating the size distribution of the cells. The computed permeability curves here have been derived from the former, arguing that a large neck implies a large cell, although both reason and experimental evidence deny a strict proportionality. Since we handed in the present curves for publication, rising moisture characteristics have been taken and used for the calculation of permeability, and have yielded permeability-moisture content curves which agree with experiment rather better than does that published here.

II. BOTANICAL ASPECTS

MECHANISM OF MOVEMENT OF SOLUTIONS IN PLANTS

Introductory Paper

By R. D. Preston

Received 3rd March, 1948

It has been an open question whether biology is to be classed with the more formal sciences of physics and chemistry and, indeed, whether it is to be classed as a science at all and it is therefore a source of satisfaction that the Faraday Society has arranged this conference in such a way as to include one of the more fundamental aspects of plant physiology and certainly the one with the longest history. The water relations of plants have been a subject of enquiry among naturalists, botanists and physiologists as well as among physicists for at least 200 years and have been the direct progenitor of the study of osmosis following the first observations of plasmolysis made at the turn of this century by de Vries. During that time the physico-chemical aspects of water entry into a plant, of the distribution of water in plants and of its exit from plants in the form of vapour, have received intensive consideration. It is perhaps rather remarkable that after the original conception put forward in the early years of this century, that protoplasm behaves as a passive semipermeable membrane, no attempt to substantiate this " classical " view by experimental evidence was made until the work of Bennet-Clark and his collaborators in 1936. This is particularly strange since it was clear almost from the first that the entry of mineral salts does not follow the course that the laws of diffusion would lead one to expect. The work of Bennet-Clark, however, called immediate and forceful attention to the complexity of water relations, and since that time the various aspects of non-osmotic flow in plant cells has received considerable attention and to-day we are to hear something of the position which these newer studies have reached. Undoubtedly movement of water or of aqueous solutions in tissues cannot be understood in any detail until the phenomena associated with single cells are resolved, but it is well at this time to bring under review the special problems which the complexity of tissues superimposes on those of single cells. The entry of water into, and passage through, the root system involves mechanisms upon the nature of which there is no settled opinion. To this study, Lundegårdh has made notable contributions; but nevertheless it cannot be said that his interpretation in terms of " anion respiration " is universally accepted, though a general connection of water movement with respiration is indicated rather clearly in plant, as in animal, cells. Similarly, movement of solutions through the specialised tissues of the phloem involves again special mechanisms and we welcome therefore the discussion by Crafts, who has over many years contributed notably to our knowledge in this field. As regards the loss of water by plants, it is very probable that in the bulk of the higher plants water evaporation provides the force which drives water from the roots to the leaves and the question of control of this transpiration is therefore a matter of some moment. The stomatal mechanism lies clearly outside our present field of enquiry, but the question of control of transpiration by "incipient drying" of the cell membranes of leaf cells is clearly within the scope of this conference, and we are happy that van den Honert has drawn on his wide experience to bring clearly under review the various physical factors with which control of transpiration rates may be associated. It is to be regretted that, owing to an unfortunate accident in my own laboratory, we have no direct statements concerning the question of sap ascent, but it is to be hoped that van den Honert's paper may lead to some discussion on this point. Finally, the papers by Lewis and Fogg are welcome reminders that we must not overlook the complexities in the evaporating surfaces of leaves.

It is well beyond my province, and indeed my capabilities, to discuss at this time any of the numerous, and often controversial, physico-chemical approaches made in this series of papers, and it seems to me that my function is rather to give to the physical chemists, whose help we are hereby soliciting, some understanding of the general botanical background.

Living plant cells consist of protoplasm containing one or more vacuoles (aqueous solution of salts, sugars, proteins, etc.); in the adult cell it forms an envelope of thickness varying from cell to cell, completely surrounding a large central vacuole. On the outside the protoplasm is itself surrounded by a wall composed largely of cellulose and pectin, though in a few living cells lignin may also be incorporated. The barriers to water entry into the cytoplasm are therefore the cell wall and the protoplasm-wall interface, which is probably a multimolecular protein-lipoid complex [1] [2] stabilised by an atmosphere of ions (see, e.g., [3]), and into the vacuole the additional barriers associated with the structure of the protoplasm and of the protoplasm-vacuole interface. All these may be regarded as porous bodies in so far as penetration by water is concerned. In general, the resistance of the cell wall to water movement is so small in relation to that offered by protoplasm that it may be disregarded, though the wall has undoubtedly a part of some considerable importance to play in virtue of the resistance it offers to increase in cell volume. Classically, the driving pressure involved in water intake in a cell placed in water was the difference between the osmotic pressure of the vacuolar sap and the hydrostatic pressure set up by the resistance to extension of the cell wall. This net force is the so-called suction pressure and it would follow that a cell placed in a solution should so adjust itself that its suction pressure equals the osmotic pressure of the solution. The suction pressure should therefore equal the osmotic pressure of the vacuolar sap when the cell is plasmolysed (i.e., the hydrostatic pressure is zero), and zero when in equilibrium with pure water. It is on discussion of the former case that the work of Bennet-Clark is founded. As regards the latter, it is now quite clear that plant cells continue to take up water long after equilibrium might have been expected,[4] [5a] [5c] the suction pressure in, for instance, potato discs being still about 2 atm. even after eight days' immersion. This long-continued water uptake occurs only in the presence of oxygen so that, as was in fact indicated some time ago,[6] the respiratory mechanism is in some way involved. Neither the breakdown of starch to sugar nor the formation of new cells by division can account quantitatively for the effect,[5c] and this is equally clear in leaves,[7] where a similar phenomenon occurs. Attempts have been made [7] [8] to explain the effect as a change in hydration of the protoplasmic colloids on the assumption that water uptake reflects cytoplasmic swelling and not actual penetration into the vacuole, and this may obviously have a part to play. For this and other reasons which will be discussed by Bennet-Clark, Mason and Phillis reject the classical theory of cell water reactions. On the other hand, many workers (e.g., [5b]) prefer to conceive ot this non-osmotic flow as electro-osmosis involving the ζ-potential of the membranes and a potential difference E between the inner and outer surface caused primarily by the diffusion of cations to which the (negatively charged) protoplasm is permeable. This would readily harmonise with the respiration-dependence of water uptake, if it could be demonstrated, as appears likely in, e.g., frog's skin, that the potentials are maintained by energy transfer in the cell. The actual rate of water entry would then depend, not only on the product $E\zeta$ but on the size and distribution of the pores. Nothing unfortunately is known concerning pore size in protoplasm or in the membranes, but, whether the proteins of protoplasm are regarded as fibrillar (e.g.,[9]) or globular (e.g., the vitaids of Lepeschkin [10]), or a mixture of both, it is clear that pore size and its distribution will vary not only from cell to cell but in one and the same cell at different stages, and, in particular, a growing, or even a potentially growing, cell may have a configuration different from that in an adult cell. This is clear even from considerations of the molecular structure of the wall if we grant that structure in the wall reflects structure in the cytoplasm-wall interface,[11b] [11c] and is indicated in the work of Lepeschkin [10] using the Plotnikow effect. There is, therefore, plenty of scope for wide variations in rates of flow such as are actually observed.[2] In spite of this, it seems unlikely that electro-osmotic effect can account in any quantitative sense for water intake.

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[1] Danielli and Davson, *J. Cell. Comp. Physiol.*, 1935, **5**, 495; Davson and Danielli, *The Permeability of Natural Membranes* (University Press, Cambridge, 1943).

[2] Höber, *Physical Chemistry of Cells and Tissues* (Churchill, London, 1947).

[3] van Reine, *Rev. trav. bot. néerlandais*, 1935, **22**, 467.

[4] Reinders, *Proc. Kon. Med. Akad. Wet.*, 1938, **41**, No. 7.

[5] Brauner and Brauner, (*a*) *Rev. fac. Sci. Univ. Istanbul B*, 1940, **5**, 266; (*b*) *New Phytol.*, 1940, **9**, 104; (*c*) *Rev. fac. Sci. Univ. Istanbul B*, 1943, **8**, 30; (*d*) Brauner, *Rev. fac. Sci. Univ. Istanbul B*, 1945, **10**, 1.

[6] Steward, *Proc. Leeds Phil. Soc.*, 1928, **1**, 258.

[7] Mason and Phillis, *Ann. Bot.*, *N.S.*, 1942, **6**, 443.

[8] Phillis and Mason, *Ann. Bot.*, *N.S.*, 1943, **7**, 147.

Turning to the question of active water movement through roots, the one central fact which still defeats explanation is the polar movement from outside to inside. There is a school of thought, chiefly in America (e.g., Eaton [12]) which treats the problem as purely osmotic, the driving force causing polar movement being the osmotic pressure difference between the sap in the central (dead) vessels and the external solution. It seems clear, however, that roots can exude sap when the external solution is osmotically more concentrated than the sap, as shown, among others, by Lundegårdh. Under these conditions the problem is how to pass water from the living cell of the root adjacent to a dead vessel into the vessel and it is difficult to see how anion permeability can effect such transfer. Possibly electro-osmotic effects are involved.

While, however, exudation from roots is of considerable interest, its importance in driving water up the stems of plants should not be overrated. Although roots growing in nutrient solutions can exert pressures of over 7 atm.,[13] it is seldom that values greater than 1–2 atm. are detectable in roots growing in soil; and particularly in trees, where the problems of sap ascent are extreme, the contents of the vessels (long, open capillary tubes in the xylem, the tissue along which water passes) are demonstrably under tension. It is generally agreed, therefore, that the sap is drawn upwards from above, rather than pushed from below, the pressure involved developing from the evaporation from the leaves through the suction pressure of the living mesophyll cells of the leaf in contact with the veins. It is further generally considered that the tensions thus developed are transmitted to the roots through long, continuous water columns in the vessels * so that there would exist in the xylem long threads of water under tensions which have been estimated, from the comparisons with the rate of flow of water through stems under the action of a suction pump, as of the order of 20 atm. This forms the so-called cohesion theory of Dixon and Joly, and Askenasy. Physically, however, there seems grave reason to doubt whether these liquid columns could long remain coherent and it seems inevitable that bubbles of water vapour would develop and expand, throwing the vessel out of action as a water conductor. Some time ago, in fact, it was shown [11a] that the majority of the vessels do probably contain gas, not liquid water, under pressures ranging from 0·4 to 0·9 atm. and that the only vessels which could contain continuous water are those which have just developed, lying therefore on the outer surface of the wood, and even there no tensions could be detected greater than about 3 atm. Huber and his co-workers (see, e.g., [14]) have estimated, using their thermoelectric method, that in ring-porous trees water moves upwards in the vessels at rates which can reach values slightly in excess of 40 m./hr. It is to be noted particularly that such figures refer only to the *outermost* surface of the wood. Taking a tree, say, 20 m. high, then in a vessel 0·1 mm. diam. this would involve a tension difference between the two ends of a vessel of the order of 2 atm., assuming Poiseuille's law to hold. If the cohesion theory is to be retained, and it is difficult to conceive of water movement *except* as liquid in the lumina of vessels, then it would seem that only the outer vessels are active ; that as they age their columns break and their conducting function is taken over by the newer cells to the outside. The most significant observation which seems yet to have been made in this regard is that if the trunk of a tree is sawn through more than half-way from one side, and again from the other side a little lower down, then the tree survives, although *all* the putative water columns are broken. It should be noted that if, in fact, the only vessels which conduct water are those newly formed, then it is after all possible that the stem is not entirely passive.

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[9] Frey-Wyssling, *Submikroskopische Morphologie des Protoplasmas u. seiner Derivate* (Berlin, 1938).

[10] Lepeschkin, *Protoplasma*, 1940, **34**, 161; *Protoplasma*, 1943, **38**, 184.

[11] Preston, (*a*) *Ann. Bot., N.S.*, 1938, **2**, 1; (*b*) *Nature*, 1941, **147**, 710; (*c*) *Proc. Roy. Soc. B*, 1947, **134**, 202.

[12] Eaton, *Amer. J. Bot.*, 1943, **30**, 663.

[13] White, *Amer. J. Bot.*, 1938, **25**, 223.

* I am considering in the following the anatomically simplest case of the ring porous dicotyledons.

Turning finally to the movement of solutions down the phloem (the inner face of the bark in trees), the difficulty here is that the movement of sugars, for instance, occurs some thousand times faster than it could by simple diffusion. The path of movement is almost certainly the sieve tubes—rather wide cells joined longitudinally end to end, whose end walls are perforated by a number of pores—and it is clear that along these channels diffusion alone is quite inadequate. The explanations which have been offered fall into two categories—one, that the movement is still diffusion, i.e., movement of individual molecules, but occurs in the cytoplasm-wall interface following the original observations of Schumaker with fluorescein, and the other, that the movement is a mass movement of solutions. In this latter category falls the suggestions of Curtis [15] that the sugar solution is distributed through each sieve tube element by protoplasmic streaming, diffusion being involved only along the pores in the end walls, and of Münch [16] that mass movement occurs along the whole file of sieve tube elements under the influence of a higher hydrostatic pressure set up at the upper end of the file, in the leaves, by the high sugar concentration in the cells of the leaf mesophyll. The critical observation here, which any theory of movement must take into account, is that cut plants do not exude any detectable amounts of sugar when their cut ends are placed in water.

To summarise, then, the centres of interest with which modern work is in the main concerned are four. Firstly, the nature of the non-osmotic mechanism involved in water uptake by cells ; secondly, the cause of polar movement of water through the tissues of roots and its connection with the movement of mineral nutrients ; thirdly, the question of the stability of water under tension in capillaries ; and finally, the physico-chemical principles underlying the rapid movement of aqueous solutions in plants. In putting the issues squarely before physical chemists, as will be done in the papers which follow, it is certain that the botanists have much to gain ; and if the interest of physical chemists is aroused in the complex problems involved then our purpose will be achieved.

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[14] Huber and Schmidt, *Ber. deutsch. bot. Ges.*, 1937, **55**, 514 ; *Tharandta foret. Jahrb.*, 1937, **87**, 369.

[15] Curtis, *The Translocation of Solutes in Plants* (McGraw Hill, 1935).

[16] Münch, *Der Stoffbewegung in den Pflanzen* (Jena, 1930).

NON-OSMOTIC WATER MOVEMENT IN PLANT CELLS

By T. A. Bennet-Clark

Received 1st March, 1948

A vacuolated plant cell when immersed in water attains a fixed size and in this equilibrium condition the solution inside the vacuole is compressed by the stretched cellulose cell wall. According to the classical hypothesis of cell water relations, the excess hydrostatic pressure of this solution equals its osmotic pressure, and, since it is also postulated that the protoplast membrane is semipermeable, the chemical potential of water in the vacuole and in the pure water phase outside are equal and no flow across the membrane occurs.

Attempts to confirm this view by direct experimentation have been made in the last 15 years in many laboratories.[1 2 3 4 5 6 7 8] Direct estimates of the excess internal hydrostatic pressure (H.P.) by mechanical means cannot be obtained with most cells or tissues because of the injuries which they suffer during experimentation. The tissues of thin and smooth leaves can, however, be compressed without very extensive injury. Fig. 1 shows the relation between volume of water expressed from leaves and the excess hydrostatic pressure resulting from application of a load normal to the leaf surface. The intercept of this curve on the abscissa gives an estimate of the excess H.P. at full turgor.

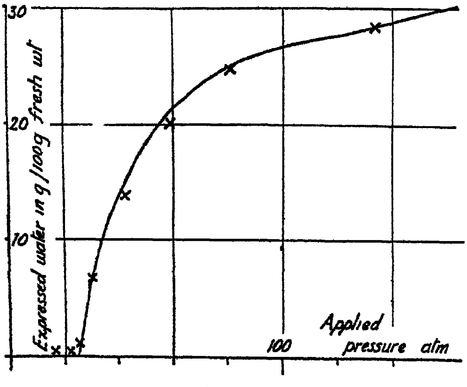

Fig. 1.

An estimate of this function can also be made by causing outflow of water from the cell by surrounding it with a solution of a non-permeating substance of sufficiently high osmotic pressure (O.P.). These so-called plasmolytic methods yield estimates of the H.P. at full turgor which are remarkably close to those determined by direct mechanical means.

One can express sap, which is regarded as closely similar in composition to the vacuolar sap from the killed tissue, and the depression of the freezing point of this sap gives a relatively accurate estimate of its O.P. The O.P. so determined is found to be markedly different from the H.P. determined mechanically or by plasmolytic methods. Results obtained in a number of laboratories confirm the absence of agreement, and some typical results are given in Table I.

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[1] Bennet-Clark and Bexon, *New Phytol.*, 1940, **39**, 337.

[2] Bennet-Clark and Bexon, *New Phytol.*, 1946, **45**, 5.

[3] Bennet-Clark, Greenwood and Barker, *New Phytol.*, 1936, **35**, 277.

[4] Brauner and Hasman, *Rev. Fac. Sci. Univ., Istanbul B*, 1947, **12**, 210.

[5] Buhmann, *Protoplasma*, 1935, **23**, 579.

[6] Currier, *Amer. J. Bot.*, 1944, **31**, 378.

[7] Eaton, *Amer. J. Bot.*, 1943, **30**, 663.

[8] Overbeek, *Amer. J. Bot.*, 1942, **29**, 677.

Two types of explanation of these discrepancies have been offered: one (the present writer's) was that the internal hydrostatic pressure was due in part to an "active pumping" of water into the vacuoles by the living protoplasts, a process which was compared with the quite definitely established active secretion of ions across the living protoplast. The other type of explanation regards the estimated values of O.P., or H.P. or both, as erroneous or faultily interpreted and considers that the true O.P. and excess H.P., if these were determinable, would be exactly equal.

TABLE I

Plant tissue and author	Hydrostatic pressure by plasmolysis or mechanically	Osmotic pressure cryoscopically	Remarks
Fagus leaf			
Dixon	—	12	Tree in Dublin
Ursprung ..	35–40	—	Tree in Freiburg
B.-C. and B ..	20–35	8	Alleged vacuolar sap
		17	Total expressed sap + solutes.
Beetroot			
Levitt . ..	10·7	10·5	
B.-C. *et al* ..	22·3	15·5	Different varieties
	17·5	12·0	
	12·0	9·5	
Rhubarb petiole			
B.-C. *et al.* ..	7·7	7·5	
Gossypium leaf			
Mason and Phillis	22·8	2·4	Possibly water filtered through cytoplasm
		15·0	Calculated from figure above and O.P. of alleged cytoplasmic sap.
Roberts and Styles			
Podocarpus salignus	25·1	20·4	
Araucaria excelsa	38·0	25·4	

The observed discrepancies noted in Table I range from several atmospheres to virtually zero in a range of different tissues, which can be explained as due to variability in the errors or variability in the secretory activity of the living cells. Most of the investigators have been very fully aware of the sources of error noted below and have attempted to eliminate them.

(*a*) The sap used for cryoscopic determinations of O.P. may be more dilute than true vacuolar sap owing to admixture with water or dilute solution filtered through undamaged semipermeable protoplasts; or it may be diluted by admixture with water expressed from the cytoplasm or cell walls (Currier [6]); or it may be diluted by reason of adsorption of vacuolar contents on protein or on cellulose material of cytoplasm and cell wall. The first possibility is eliminated (at least in the writer's work) by freezing the tissue in solid CO_2 before expression of sap. The second possibility is clearly of importance where the cytoplasm/vacuole volume is large. Where it is small, as in beetroot tissues (Currier [6], Bennet-Clark *et al.*[8]) in which this ratio may be from 0·03–0·005, water pressed from the cytoplasm must clearly have a nearly negligible effect on the concentration of expressed sap. The magnitude of the effect produced by the adsorptive capacity of cell wall and protein of the tissue is harder to assess but it appears likely to be small.

(*b*) The plasmolytically-determined excess H.P. is liable to be too large if the first traces of plasmolysis are not noticed, or if they are obscured by the adherence of protoplast to cell wall, which will result in a dragging-in of the cell wall instead of the separation of protoplast from cell wall; such a caving-in of the wall is not easy to detect, but it occurs to a negligible extent in small or relatively thick-walled cells. It has been shown to be negligible in beet by the writer by comparing values of the H.P. based on observations of O.P. required just to produce recovery from plasmolysis, with O.P. required to produce limiting plasmolysis.

(*c*) The plasmolytic value may be too large if the plasmolyticum penetrates through the protoplast into the vacuole. Occurrence of such penetration is, however, revealed by noting whether the vacuole volume of a cell immersed in plasmolyticum increases with time. Large non-polar molecules and ions have been shown to enter relatively slowly or not at all.

(*d*) When the cell walls of a tissue are very extensible, the H.P. at full turgor will be smaller than the external balancing O.P. at limiting plasmolysis by the fraction V_s/V_t, where these represent volumes at limit-plasmolysis and full turgor respectively.

These possible sources of error were carefully considered and attempts made to eliminate or make due allowance for them. There remained, however, considerable divergence between determined O.P. and H.P. of cell contents at full turgor.

The view that this difference is due to "active secretion" seemed reasonable enough until Levitt[9] pointed out the correct method for calculating the energy requirement for maintenance of an internal excess H.P. by "secretion." He points out that the work done, W, is given by

$$W = pavt,$$

where p is the H.P. due to secretion in dynes/cm.^{2} (i.e., atm. × 10^6), a is the area across which secretion occurs, v is the velocity of diffusion of water outwards through the protoplast due to the excess internal H.P. and t is the time. If the internal H.P. is to be maintained, the mechanism must pump water in as rapidly as it is caused to diffuse out by the excess internal H.P. We can assign numerical values to these terms.

The secretion pressure is usually between 0 and 5 atm. in beet; the area per gram of tissue (specific area A) is of the order of 240 cm.^{2}. The velocity, v, for a given secretion pressure can be obtained if the water permeability is known. Permeability is generally given in μ/hr./atm. Levitt cites from certain published figures, 20×10^{-4} cm./hr./atm. as a reasonable value. So the work done in maintaining a secretion pressure of 5 atm. is

$$W = 5 \times 10^6 \, . \, 240 \, . \, 100 \times 10^{-4} = 12 \times 10^6 \text{ ergs/g./hr.}$$

The heat of combustion of glucose is 3·75 cal./mg. or 15×10^7 ergs/mg., and about 0·2 mg. glucose is consumed per gram of tissue per hour. The work done in secretion is 12×10^6 ergs/g./hr. and that available from respiration only 30×10^6 ergs/g./hr. So as Levitt states, it looks at first as though there is quite inadequate energy supply.

There is, however, great doubt attaching to the assigned magnitude for the permeability of 20×10^{-4} cm./hr./atm. Huber and Höfler obtained a value of this order (actually 33×10^{-4}) by observing rate of shrinkage of cells of *Salvinia* immersed in various plasmolytica. These were long cylindrical cells with lengths 8–12 times their diameters. The protoplasts on plasmolysis are found to be cylinders with hemispherical ends. Huber

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[9] Levitt, *Plant Physiol.*, 1947, **22**, 514.

and Höfler[10] found that these long cylinders frequently broke into two parts of very unequal size and when this happened the rate of shrinkage of the two parts was roughly equal (expressed as water loss/unit gradient/min./part-cell), although the surface area of the larger segment may greatly exceed that of the smaller. The only simple explanation of the data and that accepted by Huber and Höfler is that almost all the water enters the plasmolysing protoplasts through the hemispherical ends which have separated from the cell walls. Their permeability constant (33μ/hr./atm.) is calculated on this assumption; clearly, if one were to assume equal outflow over the whole surface which is 10 times larger, the permeability would be $\frac{1}{10}$ of the figure cited above.

But it is also clear that, if almost all the water leaving the shrinking protoplast goes through the hemispherical ends, the part which is still adherent to the cell walls must have a permeability considerably less than $\frac{1}{10}$ of the determined permeability of the hemispherical ends. A permeability of the adherent portion equal to 0·01 of that of the ends would still permit 10 % of the total outflowing water to pass through the adherent portions. It seems likely then that the figure for the velocity, v, in the expression, $W = pavt$, is 100 to 1000 times too large for a normal intact cell. Substitution of a correct value would reduce the work done in maintenance of the secretion pressure to 12×10^3 or 10^4 ergs with respiratory energy totalling 30×10^6, of which clearly only a small fraction could possibly be available for "secretion." Figures for the permeability of the plant protoplast given by other workers all refer to protoplasts detached from cell walls; for example, isolated onion protoplasts 20 μ/hr./atm. (Levitt et al.[11]), *Fucus* eggs 10–20 μ/hr./atm. (Resühr[12]). It is important to attempt to evaluate the permeability of the adherent protoplast and to find out something of the causation of permeability differences occurring when the protoplast becomes detached. No precise data are available at present. If a secreting mechanism is present it can only be effective in producing a high excess H.P. when the permeability is low.

Other water-secreting activities are claimed to occur in certain plant tissues. An excess H.P. develops in the xylem of roots which exceeds the O.P. of the xylem contents if the roots are respiring normally, but this secretion pressure falls to zero if respiration is interfered with by poisons or removal of oxygen. One proposed mechanism of water secretion is electro-osmosis, or possibly, one should say, anomalous osmosis.

The relation between electro-osmotic flow, or pressure generated when flow is prevented, and field strength, pore size and *zeta*-potential and viscosity have been worked out in classical studies of Helmholtz and Smoluchowski for those conditions where the pores are large in diameter relative to atomic dimensions. There are no data, theoretical or experimental, for the system in which a bimolecular (or paucimolecular) oil-film is placed transversely to an electric field. Since bio-electric potentials of the order of up to 50 mv. have been observed between the inner and outer faces of the protoplasts of vacuolate plant cells and the thickness of the insulating plasma membrane is of the order of 50×10^{-8} cm., the field strength is possibly very great. Plant physiologists hope that this theoretical problem may be taken up by physical chemists.

Attempts have been made by the writer and by Brauner[4] to obtain evidence on the possibility of an electro-osmotic component of the water-intake mechanism of plant cells by comparing effects of non-electrolytes and electrolytes in producing shrinkage of tissues. The writer's procedure was to transfer cells plasmolysed in one solution (onion epidermis commonly used) to another having the same O.P. The expectation from the classical theory, that there would be no change in vacuole volume provided that the solutes were non-permeating, is not realised. Fig. 2 shows the sort of results obtained; the equilibrium volume of the vacuole in KCl is smaller than in isotonic sucrose; a very striking increase in volume followed by a decrease to the equilibrium value occurs when cells are transferred from electrolyte to non-electrolyte and a similar reverse change occurs on return to isotonic electrolyte.

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[10] Huber and Höfler, *J. wiss. Bot.*, 1930, **73**, 351.

[11] Levitt, Scarth and Gibbs, *Protoplasma*, 1936, **26**, 237.

[12] Resühr, *Protoplasma*, 1935, **24**, 531.

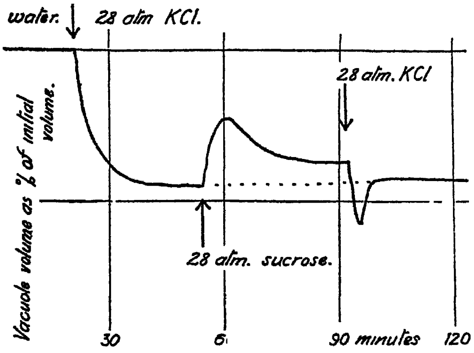

FIG. 2.

Brauner with a quite different technique showed that the extent of shrinkage in weight of potato tuber tissue was less in sucrose than in KCl solutions of equal O.P. He considered that in the KCl solutions the *zeta*-potentials in membrane pores would be much reduced and the electro-osmotic component of the water-intake mechanism would be almost eliminated. In sucrose, the existence of the electro-osmotic component caused the water content to be larger.

This explanation could be applied to the onion data, though a slightly different attempt to explain them in terms of "anomalous" electro-osmosis was originally put forward. It should be emphasised that the conception of *zeta*-potential of the pore of a membrane may not be strictly applicable to the routes by which ions and water molecules penetrate bimolecular oil-films.

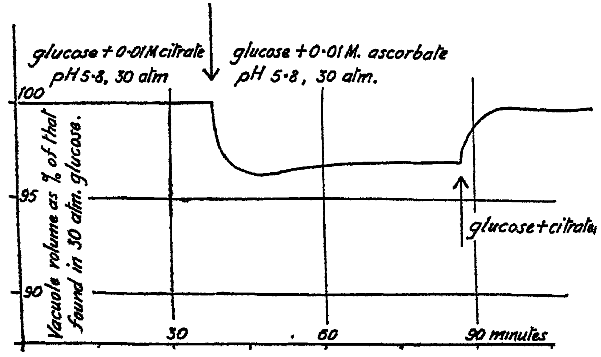

FIG. 3.

A membrane potential would need to be maintained across the protoplast if this electro-osmotic component is to be permanent, and this one expects to be generated by metabolic processes. It is a first guess that the different redox potential at the inner and outer sides of the membrane might maintain the electrical asymmetry. We are trying to eliminate this gradient by bathing the outside of tissue with ascorbic acid. The effect, as seen in Fig. 3, does seem to indicate a reduced water-intake activity induced by such treatment of beet tissue, but the interpretation of this effect is still difficult since ascorbic-oxidase poisons seem to have little effect on the phenomenon.

It is still by no means certain to what extent secretory activities influence water movements through plant tissue. The writer considers that the evidence, on the whole, supports the view that secretion across the cytoplasm of individual cells occurs, the excess hydrostatic pressure or negative diffusion gradient generated will depend on the water permeability of the protoplast and one can expect this to be very small in the case of plasmolysed protoplasts whose permeabilities are large. The adherent protoplast will be capable of maintaining much larger negative gradients. Adequate discussion must await a more complete theory of phenomena of diffusion through oil-films.

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ON THE MECHANISM OF ACTIVE MOVEMENT OF WATER AND SOLUTES THROUGH PLANT ROOTS

By H. Lundegårdh

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The transport of water against an osmotic gradient is a fundamentally important process in the life of cells and organisms. The bleeding of a decapitated plant is the visible sign of a mechanism which pumps water and solutes from the medium surrounding the roots to the upper parts. The belief of several investigators that water is pumped into the roots owing to an osmotic suction from the sap (which always holds salts) is contradicted by the fact that the bleeding can continue if the osmotic value of the medium is raised above the osmotic value of the ascending sap.[1]

The force by which water is exuded from the top of the root system is determined by the osmotic value of the medium at which the bleeding stops.[2] The relation between the intensity of the bleeding (Q = quantity of sap given off per time unit) and the osmotic value of the medium (P_0) obeys the empirical formula $Q = k(\sqrt{P_i} - \sqrt{P_0})$. In this formula, k is a constant and P_i is the " power of bleeding." At Q = zero, $P_i = P_0$.

The movement of water against an osmotic gradient can be brought about in several ways. Potential differences may be a source of energy, e.g., in the phenomenon of electro-endosmosis. Owing to the presence of potential differences at protoplasmic interfaces,[3] such phenomena probably are very common in the organism, but they are certainly not responsible for the sap movement from the roots. Another source of energy is the respiration mechanism transporting salt ions (" anion respiration ") because OH ions may be transported simultaneously with anions of acids. But the low dissociation of water holds this ionic transport of water on a very low level. Most cases of real sap movement no doubt are conducted by osmotic forces.

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[1] Lundegårdh, *Arkiv. Bot. Kungl Svenska Vet. Akad.*, 1943, **31A**, Nr. 2.

[2] Lundegårdh, *Arkiv. Bot. Kungl Svenska Vet. Akad.*, 1945, **32A**, Nr. 12.

[3] Lundegårdh, *Ann. Agric. Coll., Sweden*, 1940, **8**, 233.

The diagram in Fig. 1 illustrates the osmotic conditions of the plant cell The right limb of the U-tube represents an osmotic cell, covered by a semipermeable membrane M and closed by a piston carrying the weight T, which symbolises the turgor tension of the cell wall. The left limb of the tube contains pure water. The black dots symbolise the number *n* of osmotic particles, osmotic equilibrium being attained when so much water is sucked in through M that the osmotic pressure is balanced by T In this situation each osmotic particle is surrounded statistically by a portion *n* of the water in the cell. T being constant, water is pumped out from the cell, if the osmotic value is lowered, either by exudation of osmotic particles (Case B) or their disappearing within the cell (Case C). Both cases are realised in the bleeding of wheat roots.[2] It appears from Fig 1 that the force of bleeding is identical with the turgor pressure of the exuding cells.

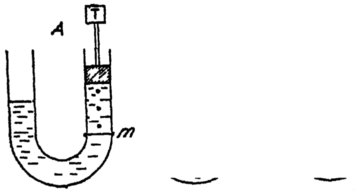

FIG. 1.—Scheme of the osmotic fundamentals of bleeding.

Fig. 1 illustrates the outgoing branch of the sap stream. But the root simultaneously pumps in water (and solutes) from the medium. This process, of course, is the reverse of the former one, viz., each particle absorbed by a turgescent cell with elastic wall is accompanied by a quantity of water which corresponds to the quotient (*n* water molecules) / (*n* osmotic particles) at equilibrium. The quotient varies approximately inversely as the osmotic pressure of the cell. An exact treatment of the problem must include corrections for the elasticity of the wall, van der Waals' forces, hydration of the protoplasm, etc., but this is not needed for our presentation of the fundamentals of the problem. It is sufficient to know that each osmotic particle taken up, or given off, from an osmotic cell carries with itself a quantity of water which is large, if the cell has a low pressure, and is small, if the osmotic pressure is high.

The continuous flow of sap in one direction necessarily implies a sort of valve mechanism, viz., an anisotropic structure of the tissues Water must be taken in at one side and sap given off from another. And the energy-delivering process must be in some way connected with the anisotropic structure. A large number of physiologists, from Pfeffer (1897) to Münch (1930), ascribed the one-sided flow of sap to permeability differences. If one side of a cell lets out osmotic substance, sap must be exuded from this side. This is our Case B in Fig. 1. Now a higher permeability does not necessarily mean a general leakage of solutes. It may be restricted to an increased exchange of ions from charged points of an amphoteric protoplasma membrane.[2] Or in other cases, as in the nectaries, sugar molecules may be preferably exuded.

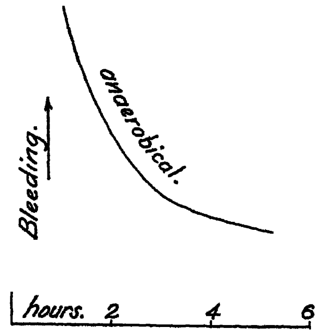

FIG. 2.—Slow decrease of the bleeding under anaerobic conditions. After (1), expt. 13

The exudation of salt ions and water in the ascending sap stream of the roots is a more passive process, because under no circumstances was the exuded sap found to be more concentrated than the cell content of the root tissue.* That no oxygen respiration is needed for the outpouring of sap may also be gathered from the fact that bleeding continues for some time from roots under anaerobic conditions or after treatment with HCN or NaN_3 (Fig. 2). The direction of the sap flow must on the other hand be guided by local differences in the permeability for solutes (Case B in Fig. 1), or for water (Case C), or for both. How the anisotropy in respect of the permeability is realised cannot be discussed here. Obviously the result would be the same, if the transverse protoplasma membranes of the conducting tissue were provided with a valve mechanism similar to the structure of those membranes which let water and solutes through more easily in one direction than in the reverse. All questions of polarity touch on these problems.

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* The terms active and passive are used in the common meaning of processes which involve an increase or a decrease of energy, respectively.

If the exudation of sap is a passive function, the ingoing flow must imply active work. Each molecule of water entering a fully turgescent cell (osmotic pressure = wall pressure) needs a supply of osmotic energy. This energy may be delivered by metabolic processes, e.g., the decomposition of one large molecule into two smaller ones within the cell, or by active absorption of solutes from the outside. Metabolic osmotic energy is produced, e.g., in the hydrolysis of starch or in the glycolysis. In photosynthesis, CO_2 is absorbed from the outside. Its reduction and condensation to sugar again releases osmotic energy. Such cases of *Druckströmung* have been discussed at length by Münch.[4]

In the roots the active pumping mechanism is connected with the absorption of salts from the medium. The anion respiration here provides the necessary energy.[2] This respiration mechanism is not restricted to the epidermis only. It works through the whole cortex and pushes anions (and consequently also cations) upwards and inwards to the same degree as salts are released from the cortex to the ascending sap stream. With continuous supply of potassium nitrate to roots of wheat, K^+ and NO_3^- are uniformly stored in a zone 30–100 mm. from the tip. Owing to the localisation of outflow of sap, preferably to a zone 10–30 mm. from the tip the NO_3^- concentrationis considerably lower here. Also the nitrate assimilation contributes to the lower level in the tip zone. If the roots are transferred to distilled water they continue to bleed a dilute salt solution, as a consequence of which the stored quantities now move down to the area of exudation (see Fig. 3) until the bleeding stops from exhaustion of salts. The intensity, however, is increased again if the root system is replaced in a salt solution.

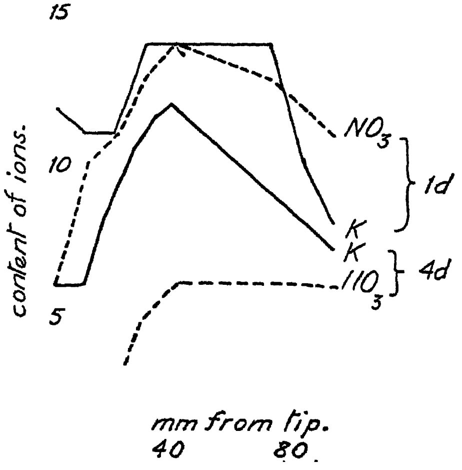

FIG. 3.—The content of K^+ and NO_3^- in different zones of wheat roots, 1 day after the change of nutrient solution, or 4 days after transfer to distilled water. After (2), Fig. 2.

The experiments quoted in Fig. 3, and the investigations of Machlis[5] on roots of barley, teach us that all cells of the cortex—and this tissue comprises *ca.* 90 % of the root mass—are provided with the mechanism of ion accumulation. As exudation occurs from and through the same cells, the balance between ingoing and outgoing solutes obviously forms a steady state and the level of accumulation is a measure of the mutual intensities of the active up-hill reaction, viz., the anion respiration, and the passive down-hill process, viz., the sap out-flow. The two counteracting groups of reactions may, of course, be tuned at different levels in different parts of the root; we already mentioned this circumstance in discussing Fig. 3.

The dominating role of the movement of salt anions is illustrated by the fact that the bleeding gradually ceases in N_2 or HCN and this is accompanied by inhibited exudation of anions. The decreasing bleeding from roots, placed in solutions of glucose, is apparently caused by the disappearance of nitrate ions—the most easily transportable ones—owing to the protein formation—from sugar and NO_3^-. The relation between the intensity and supply of salts from the exuding tissue is illustrated by a number of experiments with varying nutrition,[2] using 2–3 weeks-old seedlings of wheat.

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[4] Münch, *Die Stoffbewegungen in der Pflanze* (Jena, 1930).

[5] Machlis, *Amer. J. Bot.*, 1944, **31**, 281.

The writer previously assumed that the ascending sap was conducted in the central vessels of the stele right from the starting-point in the zone behind the growing root-tip. James and Baker several years ago [6] published some experiments, on the basis of which they developed the idea that the active sap stream from the roots is conveyed exclusively in the parenchyma, the vessels playing a more secondary role, except as channels for the transpiration stream. In order to test this hypothesis some new experiments were performed.

Transverse sections of the wheat root (see Fig. 4) show that the protoxylem is developed in the growth region, *ca.* 2–3 mm. from the tip. Also the large central lacuna, which forms a wide channel through the root, originates in this region. The large vessels of the octarch root appear at a height of some 15–20 mm., but the secondary thickening of the walls of the endodermis are not yet developed. The U-shaped thickenings appear at a height of *ca.* 30 mm. (Fig. 4 C) and are well developed at 57·5 mm. (4 D). All cells of the stele, except the eight large vessels, are living at least up to a height of 60 mm. The elements of the stele are not separated by intercellulars and the vessels are filled with water. The cortex has plenty of intercellular channels, but the transverse walls are intact, and according to the remarkable length of the cells—which makes them well adapted to conducting purposes—their tangential contact surfaces are sufficiently large to permit communication with the stele in a radial direction.

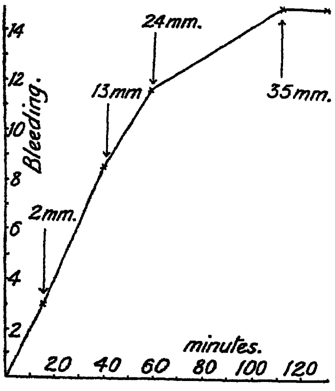

FIG. 5.—The reaction of the bleeding to cutting off parts of the root ends (method of measurement, see (2), Fig. 11). The roots were successively cut off at the height of 2, 13, 24 and 35 mm. from the tip.

The anatomical structure of the root does not give the impression that the sap stream is confined exclusively to the cortex. The carbohydrate nutrition of the root also suggests an intimate communication between the phloem of the stele and the cortex. Participation of the phloem in the ascending sap stream is very improbable, because the bleeding sap is completely devoid of organic substances, even under anaerobic conditions. The wheat root thus fits into the classical scheme of the differential function of xylem and phloem. The fact that the cortex is partly disorganised in the older parts of the root (from the zone of secondary roots upwards, e.g., in wheat at a height of *ca.* 40–50 mm.) also fails to support the belief that the elements of the stele are not endowed with the transport of bleeding sap to distant places ("long line transport"). The main question will then be the role of the cortex in the lower parts of the root.

Several authors hold the view that the growing root hairs are the chief instruments of active ion absorption. This is obviously not the case, because all cells of the cortex up to a height of at least 100 mm., together with the epidermis, accumulate salts. Root hairs can increase the surface of the root by 20 times, and growing root hairs frequently occur several centimetres from the tip, but this enlargement of the interphase between the root and the medium is primarily important for absorption from the soil. It is well known that seedlings growing in nutrient solutions behave very capriciously in respect of root hairs and that this fact does not appreciably affect the supply of nutrient ions.

In three series of experiments the bleeding was measured before and after the lower parts of roots were cut off at different heights (Fig. 5). The results are schematically summarised in Fig. 6 A and B. The cutting was made by means of scissors (A) or a razor-blade (B). In series A the removal of the growing root tips (3–5 mm.) had no effect, i.e., the bleeding continues at the same speed (i.e., 100 %).

[6] James and Baker, *New Phytol.*, 1933, **32**, 315.

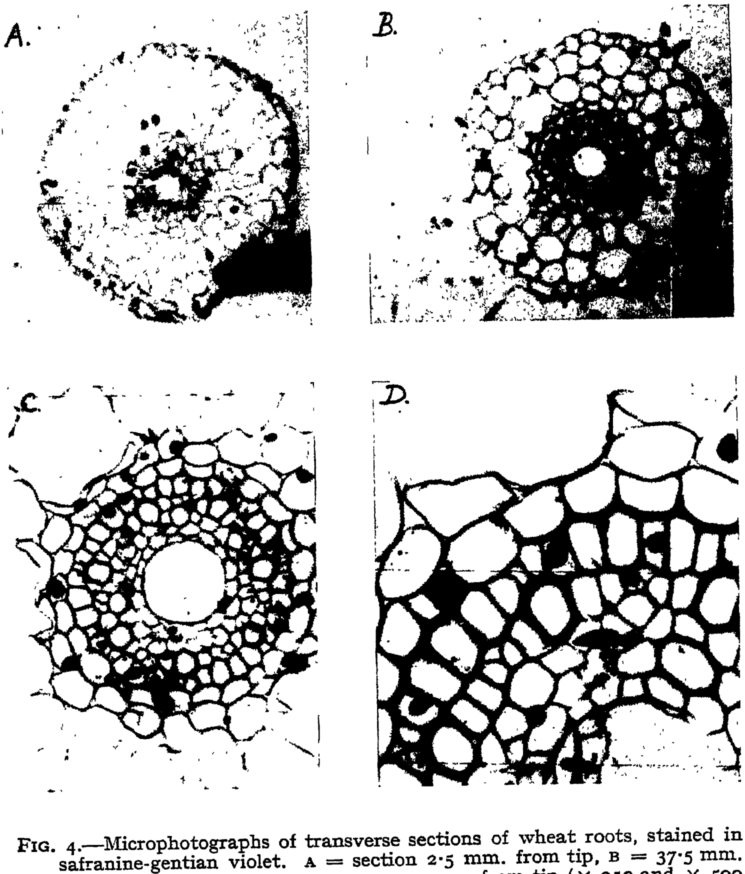

FIG. 4.—Microphotographs of transverse sections of wheat roots, stained in safranine-gentian violet. A = section 2·5 mm. from tip, B = 37·5 mm. from tip (× 100). C = 37·5, D = 57·5 mm. from tip (× 250 and × 500 resp.). Black spots = nuclei.

The removal of 15 mm. lowers the bleeding to 72 %. If 25 mm. of the root ends are cut off, on an average only 12 % of the bleeding intensity was left. Cutting off 30 mm. of the roots stops the bleeding completely. In series B the decline is more rapid; removal of the tips (5–6 mm.) caused a decrease to 76 %, at 15 mm. to 55 %, and at 20 mm. to 30 %.

The discrepancy between A and B is probably due to the fact that cutting by scissors squeezes the vessels and the central lacuna, thus impeding a back-flow of sap. A sharp razor-blade leaves the vessels open so that a part of the bleeding sap can escape the wrong way. This conclusion is supported by some experiments with the root ends killed in alcohol (Fig. 6 C). The vessels remain in this case closed completely. If 20 mm. of the ends were killed the bleeding still amounted to 45 %, whereas series B only to 30 %. These experiments support the conclusion that a minor part of the bleeding sap is conducted in the central vessels. The main part of the sap stream, however, is obviously flowing in the cortex, at least up to a height of 25 mm. The bleeding activity reaches its maximum in the zone 15–25 mm. but stops already at *ca.* 30 mm. height. This figure coincides with the first appearance of the vegetation points of the secondary roots. The cessation of the bleeding in the zones above 30 mm., after the removal of the whole root ends up to this height, is not caused by an increased back-flow through the vessels. If the secondary roots are well developed they take the main part of the bleeding (in one case 80 %), even if the main root is cut off at 30 mm.

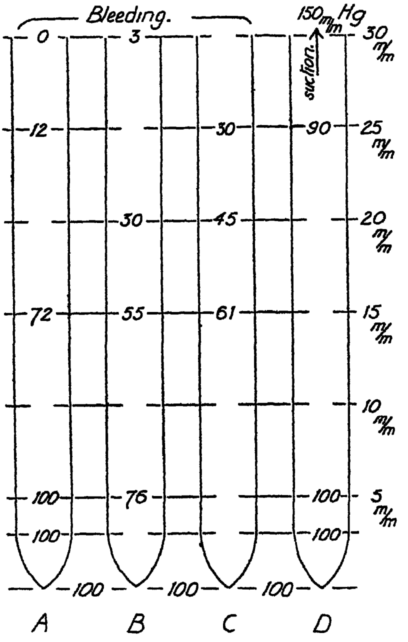

FIG. 6.

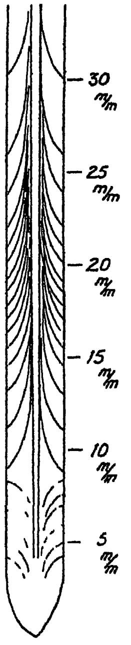

FIG. 7.

FIG. 6.—Schematic summary of four series of experiments on the bleeding of 2–3 weeks'-old wheat seedlings, taken from nutrient solutions and placed in distilled water. The roots were cut off at different heights. The corresponding change in the bleeding was calculated in % bleeding of the intact roots at the beginning of the experiments. A = roots cut with scissors, B = with razor-blade, C = the roots partly killed by alcohol, D = roots submitted to an extra suction of 150 mm. Hg.

FIG. 7.—Scheme of the probable course of active sap movement from the absorbing, surface of the root through the cortex, to the stele and to the growing tip.

The vessels of the root, including the central lacuna, form continuous capillary tubes, covering *ca.* 1–1·5 % of the total area of the transverse section (the stele.

inclusive of endodermis, covers 10 % at a height of 2·5 mm., and 15 % at 37·5 mm.). These tubes satisfy fairly high demands from the side of the transpiring leaves. Already a suction pressure of 100–170 mm. Hg accelerates the ascending stream of water several times (cp.[2]). Even if 25 mm. of the root ends are cut off, 90 % of the quantity of water, which under identical conditions is conducted through the intact root system, is sucked through (see Fig. 6 D). The small decline of 10 % is obviously caused by the omission of the active component of the "transpiration" stream.

The last-named experiments clearly show that the resistance to the bleeding stream must be very small. That so little of the bleeding sap is lost under these circumstances through the open vessels suggests that the ascending sap is largely under the influence of living cells, at least up to a height of 30 mm. The power of active transport of these elements—both in the cortex and in the stele—is lost at about 30 mm. This fact does not tell us anything about the ability of the cortex to conduct sap passively even at higher levels, but it seems more likely to assume that the ascending sap is largely brought over in the stele during its transport above the 30 mm. limit.

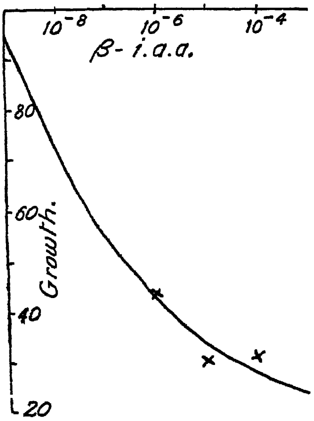

FIG. 8.—The retarding effect of β-indole acetic acid on the growth of wheat roots. The two highest concentrations (in mol./l.) as sodium salt.

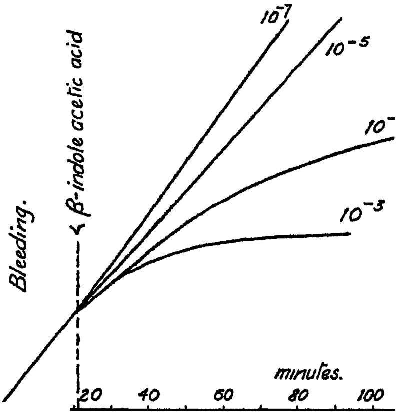

FIG. 9.—The bleeding after transfer to solutions of β-indole acetic acid (mol./l.)

The fact that the transporting power of the root tissue has its maximum—as far as the ascending sap concerns—in a zone *ca.* 15–25 mm. from the tip must be considered in the light of other facts which point to a branching-off of the stream in the direction of the apical meristem. As a matter of fact, the cutting-off of the 2–5 mm. tip zone in some experiments raised the bleeding above the value for intact roots (this was the case in the experiment shown in Fig. 5 ; the increase here amounts to 24 %). There is probably a reversal of the polarity at a height of *ca.* 5–10 mm. (see Fig. 7) so that this zone forwards salts in the apical direction, to the growing tip, a fact which is also seen in the distribution of ions (see Fig. 3).

Fig. 7 gives schematically a summary of the results of all experiments. The active absorption of ions and water is going on from *ca.* 5 mm. to *ca.* 30 mm. ; the absorption power at higher levels, up to 100 mm., does not appreciably contribute to the ascending sap stream. Near the tip zone the ingoing sap branches off in a descending stream which furnishes the meristema with salts. Some "extra water" is obviously here again released into the medium, thus working against the ascending stream if intensive growth occurs. The dominating ascending branch of the sap stream works along two gradients. The longitudinal component sends a stream upwards through the cortex, the transverse component transports salts and water to the stele and partly releases them into the vessels. To what extent the living elements (pericykel xylem parenchyma) of the stele participate in the polar movement of solutes—the phloem stream is not considered here—we do not know, but the experiments do not support the extreme hypothesis of James and Baker,[6] who deny any function of the xylem in the transport of the ascending *active* sap stream. On the other hand, the results do not support the earlier view that the stele is the tube of an osmometer, whose working body is situated near the tip of the root. The transverse component of the sap stream might be controlled by an O_2 gradient in the direction of the radius of the root,[2] [7] but there also exists a polarity in a longitudinal direction which must have other causes and an active transport of ions to the meristema of the tip. The latter branch of the longitudinal component takes only a minor fraction of the total sap, a fact which is also demonstrated by the inability of factors (e.g., *p*H), which severely affect the growth intensity, to change the course of the bleeding. The bleeding is practically independent of the *p*H down to *ca.* 3. Below this point the roots are killed after some time and this means a decrease of the bleeding at *p*H values of 2·5–2·9. The slow development of this reaction is probably due to the efficient buffering capacity of the wheat roots. As the bleeding continues some time after the death of the epidermis, this tissue and its active absorption is obviously not the site, or cause, of the sap exudation. In 10^{-4} NaOH (*p*H = *ca.* 10) the bleeding decreases to 60 % in 30 min. In this case the growth behaves similarly. The growth was measured at intervals of 4 min. by means of a film camera connected with a microscope.

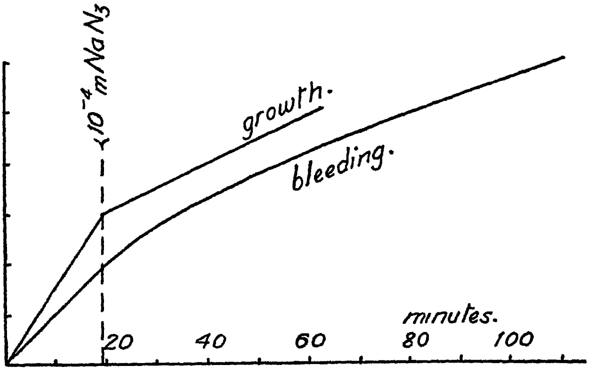

FIG. 10.—The influence of sodium azide on growth and bleeding.

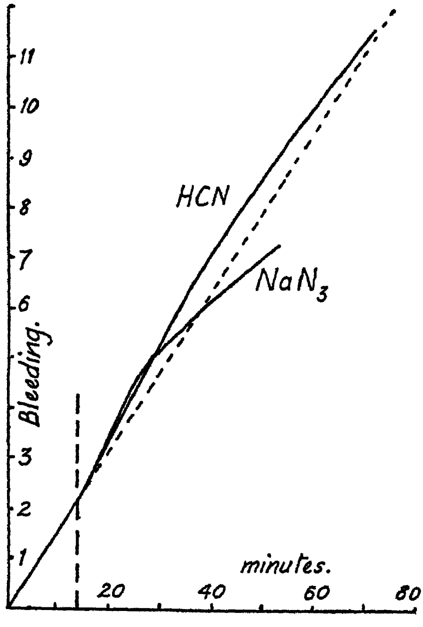

FIG 11.—The preliminary slight acceleration of the bleeding under the influence of HCN and NaN_4.

The growth of wheat roots is retarded by concentrations of β-indole acetic acid (i.a.a.) higher than *ca.* 10^{-10} mol./l. (see Fig. 8). Also the bleeding is retarded by i.a.a. but the limit is here *ca.* 10^{-6} (Fig. 9). At 10^{-7}, a slight acceleration is noticed, 10^{-4} retards strongly, and in 10^{-3} the bleeding is completely inhibited after one hour. The stronger solutions discolour the roots and severely affect the protoplasm. According to recent investigations,[8] auxin interferes in some way with the C_4 acids of the respiration mechanism. Also malonic acid, a specific inhibitor of the succinic acid dehydrogenase, and of the intermediate stages of respiration, does not influence the bleeding until the concentration is raised to 5×10^{-3} mol./l. at pH = 3. The comparatively slight retardation (*ca.* 60 %) of the bleeding can, of course, also depend upon the low pH Machlis,[5] one of the few who have been successful with malonic acid inhibition of plant respiration, got appreciable retardation only in concentrations above 10^{-3}.

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[7] Lundegårdh, *Nature*, 1946, **157**, 575.

These experiments, together with earlier ones concerning the bleeding under anaerobic conditions (Fig. 2), clearly show that the active sap movement in the root is regulated by the aerobic respiration of the out-grown cells. In all experiments the effect of inhibiting agents *develops slowly*, whereas, e g., the inhibition of the aerobic respiration or of the anion respiration almost immediately affects the growth (see Fig. 10) or the active transport of anions. This fact, together with the observed composition of the sap, supports the conclusion that the release of sap is an anaerobic process and that the final cessation of it is caused by the inhibition of the up-hill process, viz., the anion respiration, which furnishes the cells with the chief osmotic material. This process is checked by HCN and NaN_3 and these agents also cause an inhibition of the bleeding similar to that obtained after the exclusion of oxygen (Fig. 10, 2).

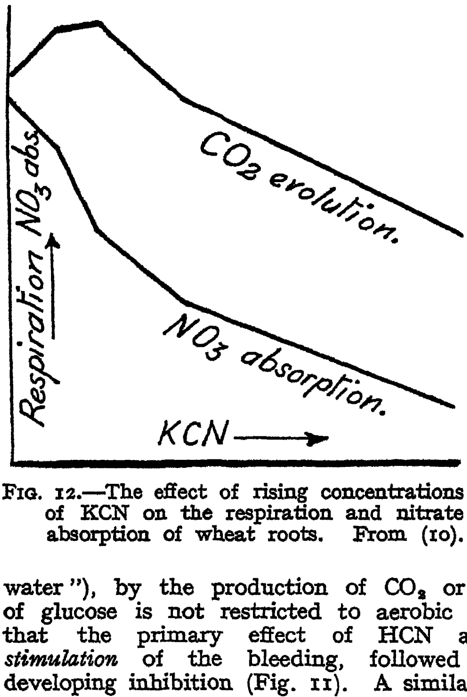

FIG. 12.—The effect of rising concentrations of KCN on the respiration and nitrate absorption of wheat roots. From (10).

The aerobic "fundamental respiration," which is not inhibited by HCN or NaN_3, can of course also supply some osmotic energy, e.g., by combustion of glucose ("extra water"), by the production of CO_2 or organic acids, etc. The transport of glucose is not restricted to aerobic conditions.[9] It deserves attention that the primary effect of HCN and NaN_3 is a slight temporary *stimulation* of the bleeding, followed by the above-mentioned slowly developing inhibition (Fig. 11). A similar effect on the respiration has been observed by the writer (see [10], Fig. 12) and Machlis.[5] The stimulation might be caused by the release of processes which are blocked by the cytochrome-cytochromeoxidase system, and which increase the exudation of "extra water" and bicarbonates of cations, which are still accessible despite the inhibited active transport of anions.

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[8] Commoner and Thimann, *J. Gen. Physiol.*, 1941, **24**, 279.

[9] Lundegårdh and Burström, *Ann. Agric. Coll., Sweden*, 1944, **12**, 51.

[10] Lundegårdh and Burström, *Biochem. Z.*, 1935, **277**, 223.

WATER TRANSPORT IN PLANTS AS A CATENARY PROCESS

BY T. H. VAN DEN HONERT

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In treatises on rates of transpiration and water transport in plants, considerations are mostly confined to a part of the system involved. Some deal with the intake of water by roots, some with the transport through the xylem, others with the transpiration from leaves and then consider the factors influencing the water transport through the respective parts. In several publications, attention is given to the resistance met by the water transport in the different parts and, sometimes, a comparison is drawn between resistances in root cells and vessels, or between that in veins and leaf parenchyma. But comparatively seldom one finds water transport treated as a whole and attention paid to the interaction of all parts of the entire system.

When I consider the transpiration stream in Phanerogamic terrestrial plants as a catenary process, I shall explicitly confine myself to the passive part of it. Active (secretion) processes will be left out of account; in addition, the correctness of the cohesion theory will be taken for granted and considerations confined to steady-state conditions. Leaf and air temperature are assumed to be equal and water is assumed to be plentiful among the roots. Cuticular transpiration will be neglected. Even with these simplifications, one does not deprive water transport of all of its problems.

In a plant, in which the transpiration stream has acquired the " steady-state " condition, the same quantity of water per hour passes successively through (*a*) the living root cells, (*b*) the xylem vessels and tracheids, (*c*) the living leaf cells, (*d*) the intercellular spaces of the leaf, the stomata and an air layer around the leaf. This part, in which water is transported in the form of water vapour, will be referred to as " the gaseous part." Through every single part, the transport is governed by a " potential difference " at either side and a resistance in between.

In the living tissues (*a*) and (*c*), the " potential difference " is evidently the difference in value of what is called by different authors suction force,[1] water-absorbing power,[2] suction pressure,[3] suction tension,[4] effective (net) osmotic pressure,[5] turgor deficit,[6] and diffusion-pressure deficit.[7] This last term seems to have some advantages as it does not refer to any special mechanism and may indicate the " water-potential deficit " of a solution, a living cell, a xylem vessel under tensile stress or a relative humidity. So I shall use it henceforth, abbreviated to D.P.D. Its value will, as usual, be expressed in atmospheres.

If, through a living tissue, water is transported under the influence of a D.P.D. gradient, it will meet a resistance. It is essentially a resistance met by fluids, when streaming through capillary tubes, which are here of colloidal dimensions. For the moment it may be left undecided whether the main transport takes place through the living protoplasts or through the cell walls.[8]

In the conducting xylem vessels and tracheids, the water moves under influence of a tensile stress. The " potential difference " is here an actual pressure or tension difference (which again may be expressed in atmospheres suction tension or D.P.D). The resistance met is of the same nature as before, but the capillaries are much wider and also many times longer.

From the interface between chlorenchyma cells and intercellular spaces up to the free circulating air around the leaf (*d*), water transport is a diffusion of water vapour. The " potential difference " here corresponds to the difference in water-vapour pressure and is usually expressed as a difference

[1] Ursprung and Blum, *Ber. deutsch Bot. Ges.*, 1916, **34**, 525; 1918, **36**, 577.
[2] Thoday, *New Phytol.*, 1918, **17**, 108.
[3] Stiles, *Biochem. J.*, 1922, **16**, 727.
[4] Beck, *Plant Physiol.*, 1928, **3**, 413.
[5] Shull, *J. Amer. Soc. Agron.*, 1930, **22**, 459; *Plant Physiol.*, 1939, **14**, 401.
[6] Curtis and Scofield, *Amer. J. Bot.*, 1931, **20**, 502.
[7] Meyer, *Bot. Rev.*, 1938, **4**, 531.
[8] Strugger, *Flora, N.F.*, 1938, **33**, 51.

in relative humidity or saturation deficit. However, for the sake of comparison, it may also be expressed in atmospheres osmotic pressure or D.P.D.[9] Even at high relative humidities, the D.P.D. values of the atmospheric air are considerable, as may appear from a few data, derived from Shull's table (Table I—temp. 20° c.).[5]

TABLE I

Relative humidity, %	D.P.D. atm.
99	13·4
97	40·6
90	140·5
80	297·5
50	924·2
10	3070·3

The rate of transport in the gaseous part is determined not only by a D.P.D. difference but also by the resistance met by the diffusing water molecules in the air. In this way the water potentials along the whole stretch of the water transport may be expressed in the same units, viz. in atmospheres D.P.D.

In a moist soil, the D.P.D. of the root environment is approximately zero. If we assume, for convenience, a relative humidity of the air of 47 %, the plant is inserted as a water conduct between two media with D.P.D. values of 0 and 1000 atm. respectively. A continuous current of water passes inside the plant from lower to higher D.P.D. values, successively through root cells, xylem, chlorenchyma and the gaseous part (including the stomata), everywhere meeting a corresponding resistance.

It was Gradmann's idea[10] to apply an analogue of Ohm's law to this water transport as a whole. It may be applied here because it is applicable, not only to an electric current, but to any process where its velocity is directly proportional to a potential difference. This is the case in a current of water through capillaries as well as in a diffusion process.

In the steady-state, the rate of water transport $\frac{dm}{dt}$ is the same in all successive parts. If we call the resistances in root cells, xylem, leaf cells and in the gaseous part R_r, R_x, R_l and R_g respectively, the D.P.D. values on either side of each respective part P_0, P_1, P_2, P_3 and P_4, we have:

$$\frac{dm}{dt} = \frac{P_1 - P_0}{R_r} = \frac{P_2 - P_1}{R_x} = \frac{P_3 - P_2}{R_l} = \frac{P_4 - P_3}{R_g}$$

The D.P.D. value in the chlorenchyma cells lining the intercellular spaces of the leaf (P_3) may seldom exceed 50 atm. So, in this instance, the D.P.D. difference between the free atmosphere and the leaf cells $P_4 - P_3$ should be 950 atm., 19 times greater than $P_3 - P_0$, the D.P.D. difference between leaf cells and soil. Gradmann drew the conclusion that R_g, the resistance in the gaseous part, had to be about 20 or more times $(R_r + R_x + R_l)$, the total sum of resistances inside the plant. The reasoning seems sound. It may be questioned, however, if it is physically justified.

Gradmann's important corollary hardly received attention. This may be due to its seeming improbability. In the first place, diffusion processes in gases proceed fairly rapidly compared to those in fluids, which are several thousand times slower. Besides, we know that the velocity of diffusion or transpiration through multiperforate films may approximate to the velocity in absence of the film.[11] [12] This easily leads to the implicit assumption that the diffusion resistance in transpiration through an epidermis with open stomata should be low or even negligible.

Such a conclusion, however, would be erroneous. For even in transpiration from a free water surface the resistance is very high, as any simple evaporation experiment may prove. Table II gives evaporation rates from a circular surface of 33 cm.², the temperature of air and water being the same. The relative humidity was measured with a Haenny hair hygrometer; the D.P.D. values were computed by interpolation from Shull's table. The influence of the size of the transpiring surface (Stefan's "diameter law," etc.) will not be considered here, as only the order of magnitude of the transpiration resistance is of interest.

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[9] Walter, *Die Hydratur der Pflanze* (Jena, 1931).

[10] Gradmann, *Jahrb. wiss. Bot.*, 1928, **69**, 1.

[11] Brown and Escombe, *Phil. Trans. Roy. Soc.*, 1900, **193**, 223.

[12] Huber, *Z. Bot.*, 1930, **23**, 839.

TABLE II.

	° C.	Relative humidity	D.P.D., atm.	Evaporation		
				mg./hr.	mg /hr.cm.²	mg./hr.cm.²atm.
Still air	15 16	76 % 52 %	364 861	86 200	2·6 6·0	0·007 0·007
Slow wind ..	15 16	76 % 52 %	364 861	360 600	10·9 18·0	0·030 0·021
Strong wind ..	16	80 %	293	1850	56·0	0·191

It will be seen that the calculated transport rates through 1 cm.² of evaporating surface per atm. D.P.D. difference are extremely low (7th column).

The evaporation resistance may be valued by comparing it to other resistances, in the same way as Huber and Höfler [13] did in the case of the filtration resistance in the protoplasm. A few data from their publication (wood protoplast of *Salvinia auriculata*) are included in Table III.

TABLE III.

Water displacement through	Displacement rate mg./cm.²hr.atm.	Relative resistance/cm.²
1 m. foliage wood	100,000	1
1 m. conifer wood	20,000	5
Protoplast Salvinia	3·3	30,000
Surface water-air—		
in still air	0·007	14,000,000
in slow wind	0·025	4,000,000
in strong wind	0·191	520,000

It will be remembered how the establishment of a relatively low water permeability of protoplasm by Huber and Höfler evoked some surprise. However, the "permeability" of a free water surface, depending on the wind velocity, appears to be 20 to 500 times smaller.

The air, adjacent to the water surface, may be considered to be in equilibrium with the water. In agreement with other authors,[14] [15] we may assume that the diffusion resistance in an adhering air layer is responsible for the relative "impermeability" of the evaporating surface. It is clear that, with increasing distance from the surface, there is a gradual transition from practically still air to freely circulating air. As an approximation, however, we may assume the presence of a stationary air-layer, inside of

[13] Huber and Höfler, *Jahrb. wiss. Bot.*, 1930, **73**, 351.

[14] Bachmann, *Planta*, 1932, **16**, 526.

[15] Welten, *Planta*, 1933, **20**, 45.

which the diffusion gradient is found, bordered by the free circulating air which is continuously renewed.

For this supposed air layer the following thickness may be calculated,* making use of the diffusion constant of water vapour in air:

Still air	10 mm.
Slow wind	2·8 mm.
Strong wind..	0·4 mm.

The thickness of the "vapour shell" in still air over an evaporating water surface, demonstrated by means of cobalt paper,[15] is, in fact, of the same order of magnitude.

The above calculation applies to isothermal evaporation (equal temperatures of water and air). In the case of leaves or filter-paper evaporimeters, in absence of radiation, the water temperature is lowered in consequence of the latent heat of evaporation. In the "steady-state," the temperature difference between air and water will correspond to a continuous heat supply from outside. This heat will be conducted through the same air layer as that through which the diffusion takes place. The first part of Taylor's hygrometer theory [16] is based upon this idea.

If the heat conductivity of air were very high, the water temperature would be practically the same as that of the air; if it were very low, the water temperature would become stationary close to the dew-point and hardly any evaporation would take place. In this last case, the evaporation rate would be determined essentially by the rate of heat conduction to the evaporation surface.

In practice, conditions will be between these extremes. In hygrometer determinations the temperature difference between wet and dry thermometer causes a decrease of the saturated water vapour pressure at the surface of the wet bulb corresponding to about 3/5 of the saturation deficit of the air. This means that the evaporation rate is roughly 2/5 of the isothermal evaporation rate at air temperature; so the evaporation resistance is increased by 5/2 due to resistance in heat conduction.

If the size of the supposed still air-layer is calculated from the temperature difference of the wet and dry bulb, the heat-conductivity constant of air and the evaporation rate, a thickness of the same order of magnitude as in the former calculation is obtained.

As argued above the rate of water transmission in isothermal evaporation is governed by a diffusion resistance of an air layer, the thickness of which was computed at 0·4–10 mm., depending on the rate of air movement.

In the case of a leaf surface the gaseous diffusion path may be subdivided into (*a*) the pores between the guard cells and (*b*) the rest of the air layer, each having its respective resistance, $R_g = R_p + R_a$. We shall assume that the open stomata occupy a surface, $q_1 = 0{\cdot}01$ or 1 % of the total surface, $q_2 = 1$; furthermore that the depth of the pores $l_1 = 0{\cdot}0005$ cm. and that of the adherent air layer $l_2 = 0{\cdot}5$ cm.

According to Fick's law the rate of diffusion is

$$\frac{dm}{dt} = Dq\frac{dc}{dx}$$

in which D is the diffusion constant of water vapour in air. If c_0 and c_1

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[16] Whipple, *Proc. Physic. Soc.*, 1933, 45, 307.

* I am indebted to Prof. Dr. C. J. F. Böttcher for his kind help in these calculations.

stand for the water vapour concentration respectively inside and outside the pores, c_2 for that in the free circulating air, we have

$$\frac{\mathrm{d}m}{\mathrm{d}t} = Dq_1\frac{c_0 - c_1}{l_1} = Dq_2\frac{c_1 - c_2}{l_2}$$

$$(c_0 - c_1)\frac{q_1}{l_1} = (c_1 - c_2)\frac{q_2}{l_2}$$

In our case, the ratio of concentration differences $= \frac{c_0 - c_1}{c_1 - c_2} = 0{\cdot}1$, so the ratio of the respective diffusion resistances $\frac{R_p}{R_a}$ will be the same. Notwithstanding the fact that the stomata when fully open occupy only 1 %

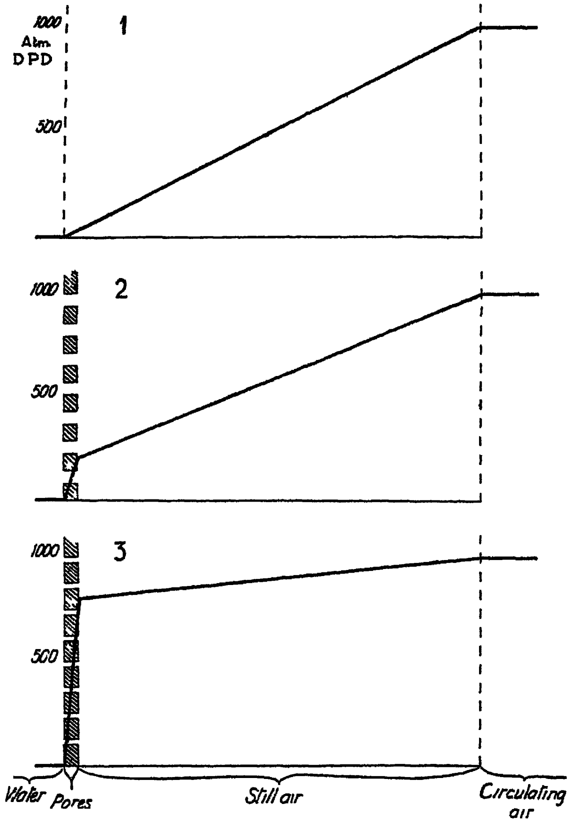

Fig 1

Showing how the D P D gradient in the adhering air layer (1) will be influenced by inserting films with different pore spaces (2 and 3) between the evaporating water surface and the air

of the total leaf surface, they offer a diffusion resistance of only 1/11 of that of the total gaseous part. It is not q_1 that counts, but $\frac{q_1}{l_1}$ and l_1 is only a few μ. So the comparatively small evaporation resistance in open stomata is not surprising. Nevertheless, the concentration *gradient* inside the pores is 100 times steeper than in the air layer. Only if $\frac{q_1}{l_1} < \frac{q_2}{l_2}$, do the stomata become really effective, e.g., by reducing q to 0·001 (0·1 % of the surface), then $\frac{c_0 - c_1}{c_1 - c_2} = \frac{R_p}{R_a} = 1$, and thus the resistance of both parts becomes equal and the evaporation rate is reduced to 11/20. So it is understandable that the main regulatory effect of stomata is found at small degrees of stomatal aperture.[17]

Especially at low degrees of stomatal aperture, c_1 will considerably deviate from c_0. Evidently it is this value of c_1, the saturation deficit or D.P.D. value at the immediate surface of the leaf, which Yarwood and Hazen (1944) call the " relative humidity of leaf surfaces." [18]

I am well aware that I have neglected several complications, e.g., the additional resistance of the " vapour-shells " over the individual pores.[11] I merely want to point out that the well-known laws of evaporation through stomata and porous films may be considered as a logical consequence of Fick's law, but only if the resistance in the adherent air layer is taken into account.

We have seen that, judging from the course of D.P.D. values throughout the plant into the air, by far the greatest resistance in the total water transport is situated in the " gaseous part " [10] and that this great resistance is a physical reality. And a very lucky one too, for it allows the plants to develop their leaf surface for photosynthetic purposes. Even though inversely proportional to the surface, the evaporation resistance remains considerable.

Now we come to an essential point. The successive transport of water through root cells, xylem, leaf cells and " gaseous part " may be considered as a catenary process. To catenary processes the general rule applies, that the " slowest " partial process practically governs the velocity of the whole. Now this is, in itself, a contradiction. For, in a " steady-state," all processes of the chain proceed at exactly the same rate. But it is evident that by the " slowest " process is meant the partial process which encounters the greatest resistance. It is usually indicated as the " master-process." This rule may be used as an approximation if one of the resistances considerably exceeds the others.

In the consecutive diffusion through pores and air layer, we have already seen an example of a simple catenary process, the master-process of which may be either the diffusion in the air layer (open stomata) or in the pores (stomata nearly closed).

Considering the whole water transport, we find a fairly great resistance in the living cells of root and leaf.[1] [18] [19] But this resistance is small compared to that in the gaseous part. That in the xylem proved to be even much smaller, at least in plants of medium size (e.g., *Helianthus annuus* [20]).

In our case, the conclusion is inevitable that the master-process is always, under any circumstance, the transport in the gaseous part. Generally it will be a diffusion process. However, under special circumstances (amphistomatous leaves, small radiation, open stomata) heat conduction through the same air layer may partly take over the role of master-process.

It is clear that the regulators of the water transport, the stomata, are inserted in the gaseous part, where they control the master-process by varying the diffusion resistance. Regulators could be nowhere else. If, for instance, the filtration resistance in the roots is increased, it will have little effect on the rate of water transport; its only effect will be an increase of D.P.D.

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[17] Stålfelt, *Planta*, 1932, **17**, 22.
[18] Yarwood and Hazen, *Amer. J. Bot.*, 1944, **31**, 129.
[19] Renner, *Jahrb. wiss. Bot.*, 1929, **70**, 805.
[20] Kramer, *Amer. J. Bot.*, 1938, **25**, 110.

in the whole plant. This and similar consequences were clearly seen by Gradmann.[10] It is difficult to see how Maximov's idea [21] of a direct regulation by root activity, without interference of the stomata, could be correct.

The decrease of evaporation resistance by enlargement of the total leaf surface may endanger the plant, unless the resistance in the roots is decreased by a proportional enlargement of the root surface. The ratio of these two surfaces must be an important factor in the water economy of the plant.

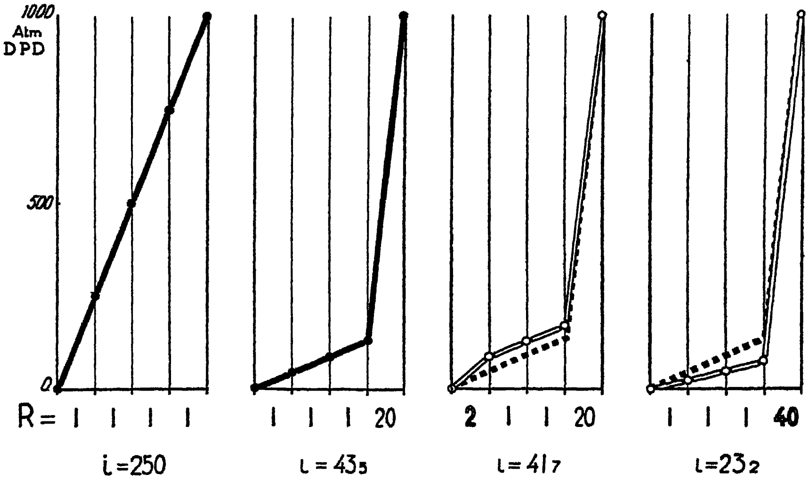

FIG 2.

Representing, as a consequence of Ohm's law, the influence of a series of four varying resistances (*R*) on the respective D.P D. values and on the rates of transport (*i*) expressed in arbitrary units.

Another deduction refers to the possible significance of incipient drying of the cell walls bordering the intercellular spaces of the leaf. To reduce materially the transpiration rate, the resistance in these single cell walls, negligible before, should increase to such an extent that it would become greater than the resistance in all the rest of the plant, which is hard to visualise.

I wonder why Gradmann's view is so little mentioned in literature. The main purpose of this paper is to call attention to his conception and some of its corollaries, which, if correct, may be considered of importance in all cases where water transport, as a whole, is concerned.

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[21] Maximov, *The Plant in Relation to Water* (London, 1929).

MOVEMENT OF MATERIALS IN PHLOEM AS INFLUENCED BY THE POROUS NATURE OF THE TISSUES

By A. S. CRAFTS

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Whereas the transport of water and salts through the xylem of plants, often as continuous, liquid columns in a tensile state, has been amply demonstrated and is widely accepted by plant physiologists, the mechanism of movement of organic materials in the phloem is still the subject of controversy. The early view, that the sieve tubes constitute files of elongate cells interconnected by open pores through which a mass flow of solution can readily take place, has proved untenable. The protoplasmic connections traversing the end walls of sieve tubes, though large and particularly prominent during certain stages of ontogeny in some species of angiosperms, have proved to be solid under normal conditions. In gymnosperms they are commonly as small in diameter as are the connections of parenchyma cells, and only their affinity for dyes during particular stages of ontogeny makes them more readily demonstrated.

Because of their structure the sieve tubes differ from xylem conductors in their properties as conduits for the movement of materials. Xylem vessels by dissolution of their end walls form pipes through which mass flow may readily take place. Files of tracheids are interrupted only by pit-closing membranes which have been demonstrated to be porous. In contrast with these, sieve tubes retain a protoplasmic sheath throughout their functional existence and perforations of their end walls are full of protoplasm. This is evidenced by the filtering action responsible for slime-plug formation, and by the occasional extrusion and inflation of the contents of sieve-plate perforations when cutting of a stem greatly steepens the pressure gradient across them.[1] Because of the nature of the phloem conductors, movement of materials through them must consist of two phases: (1) movement from end to end of each cell through the vacuolar region and (2) movement across end walls involving either alternate passage through the protoplasmic sheath, through the cellulose end wall, and again across the sheath of the next cell, or continuous passage through protoplasm from cell to cell via the protoplasmic connections. Whatever the mechanism responsible for rapid longitudinal movement of materials in the phloem, this periodic passage across end walls undoubtedly constitutes an appreciable source of resistance. During the past 20 years two general theories have been developed on the mechanism of solute movement in the phloem.[1] [2] Advocates of one propose that assimilates pass rapidly along the sieve tubes by a diffusional type of movement accelerated in some way by metabolic activity of the sieve-tube protoplasm. In such a mechanism movement of each molecular (or ionic) species would be independent of each other species and of the solvent water.

Advocates of the second or mass-flow theory propose that assimilates in solution move by a convection or pressure flow along the sieve-tube conduits. This flow is brought about by a pressure gradient between the source (leafy portion of the plant) and sink (region of utilisation of assimilates) developed osmotically and maintained by the synthesis of osmotically active solutes at the source and their oxidation or storage in the region of the sink. The various aspects of these theories have been reviewed by Curtis,[3] Mason and Phillis [4] and Crafts.[1] [2] The whole subject has been reviewed recently.[5] While these recent studies add little to the picture of diffusional movement, experiments with fluorescein, radio-phosphorus, the flower-inducing hormone, phloem-limited viruses, and a number of physiologically active chemicals, including 2 : 4-D, indicate that movement of all these materials may be correlated with food movement in the phloem. Such movement is most simply explained as a mass flow of the assimilate stream, the direction and rate of which is determined by the gradient of total osmotically active substances.

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[1] Crafts, *Amer. J. Bot.*, 1939, **26**, 172.

[2] Crafts, *Plant Physiol.*, 1938, **13**, 791.

[3] Curtis, *The Translocation of Solutes in Plants* (McGraw Hill, New York, 1935).

[4] Mason and Phillis, *Bot. Rev.*, 1937, **3**, 47.

[5] Crafts, Currier and Stocking, *Chronica Botanica* (Belmont, 1948).

In the above review [5] the statement is made, " Weaknesses of the mass-flow theories include a lack of knowledge relative to the resistance offered by the cross walls in the phloem, need for more convincing evidence for the passive function of sieve tubes. . . ." I propose in this paper to examine, in the light of modern physical chemistry, the resistance of cross walls of the phloem, and the effects of sieve-tube ontogeny on the permeability of the cytoplasm. Though it may be impossible to apply modern methods of X-ray diffraction analysis and electron microscopy to phloem tissues in their natural condition, reasoning by analogy from such studies on other tissues may throw some light on permeability of functioning phloem.

Although the young differentiating sieve tube is an active cell with streaming protoplasm of a fluid consistency, and normal semi-permeable properties, a large and conspicuous nucleus and other characteristic inclusions,[6] upon maturing a profound differentiation occurs that marks this cell type as a highly specialised structure. It is now well established that the nucleus disintegrates during maturation, that slime bodies likewise break down, in those species that have them, and finally, that the sieve-tube cytoplasm loses its semi-permeable properties and becomes highly permeable to solutes.[1 7 8 9]

Chemical studies indicate that protoplasm is a heterogeneous mixture of water, proteins, lipoids, phosphatides, sugars, salts and other compounds. Proteins make up over half of the non-aqueous composition and they are composed of amino acids united through peptide linkages into chains of considerable length. Accounting for the definite shape and size of fractionated protein molecules, and fundamentally related to the optical properties, fluid nature and motility of living protoplasm must be an ordered arrangement of polymeric structural units. There is general agreement that peptide chains form the basic units upon which the complex structure of protoplasm is built, these chains being coiled, folded and interwoven in fluid protoplasm, and arranged into more linear order when protoplasm is stretched or compressed into sheets. Accounting for the semi-permeable nature of protoplasm are the side chains on the peptide strands, the associated lipoid substances, and the complex pattern of bonded aggregates making up the living stuff. To account for the chemical and physical properties of the protein fraction, Bateman [10] concludes that the peptide chains are " folded in such a manner that the acid- and base-combining groups are either free or very weakly bonded, while the nonpolar groups are to some extent enclosed." He postulates " that many weak bonds are involved in the maintenance of a protein molecule in the native condition; a few of these may be covalent, such as sulfide or secondary peptide linkages between side chains, but most are of residual character and may be salt linkages or hydrogen bonds." Similar bonds are undoubtedly involved in the association of lipoids, minerals and water in the living protoplasm. While purified samples of proteins, lipoids and other essential components of the protoplasm may yield X-ray diffraction patterns useful in determining their physical structure, no accurate picture of the structure of living protoplasm can be formed except by analogy with those of the various non-living fractions. From these it would seem that the liquid protoplasmic layer of a plant cell in a state of rest would have the amorphous quality of a mass of randomly coiled chains, the highly individual qualities being related to specific arrangements of, and forces between, the different components. This should be characteristic of the young sieve tube at resting stages of the meristematic state.

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[6] Crafts, *Protoplasma*, 1939, **33**, 389.

[7] Crafts, *Plant Physiol.*, 1932, **7**, 183.

[8] Crafts, *Plant Physiol.*, 1933, **8**, 81.

[9] Huber and Rouschal, *Ber. deutsch. Bot. Ges.* 1938, **56**, 380.

[10] Bateman, in Höber's *Physical Chemistry of Cells and Tissues* (The Blakiston Co., Phil., 1945).

Growth in the longitudinal direction and the incidence of streaming are probably attended by an increase in order accompanying the stretching of the peptide chains. Compressional effects of turgor would have a similar influence. Such order should characterise the living protoplasm of newly expanded sieve tubes, phloem parenchyma and ray cells. What then would be the nature of the changes attending maturation of the sieve tube and how do they relate to its function in conduction ?

According to Bateman, degradation of the specific structure of proteins must involve introduction of disorder into an originally regular structure, the degraded product becoming more viscous and hence less symmetrical and less soluble. Side chains are freed, becoming more reactive, and the degree of association must shift toward an open structure. Observations previously recorded[1] prove that upon maturation of sieve-tube elements the cytoplasmic sheath changes from a fragile, fluid state to a viscous, tough, fibrous condition. This has been illustrated in cucurbits and potato.[7] [8] When mature sieve tubes are treated with 95 % alcohol under the microscope the protoplasm upon dehydration can be seen to shrink and pull away from the side walls becoming taut between the two sieve plates. Often it breaks somewhere near the centre of the cell and each portion slowly shrinks forming a torn fragment upon the sieve plate to which it is attached. Attending this change in state during maturation is an almost complete loss of staining power.

From the physico-chemical view of the properties of protoplasm the above changes probably involve a straightening and ordering of the peptide chains attended by a loosening of bonds and a loss of both the lipoid substances responsible for semi-permeability and the polar groups that determine the staining properties of the protoplasm. In the place of these would be water, mostly in the free state, the protein chains retaining certain of their para-crystalline properties. Bateman states that wet protein crystals give better X-ray photographs than dry ones and that the water is mostly in the free state. This would seem to indicate that though the highly specific molecular ordering of the young active protoplasm is lost, the straightening of the peptide chains and the freedom from interfering associated groups might leave the basic framework more clearly discernible. As a crude analogy one might suggest the skeletinisation of an animal. If the protoplasmic sheath of the mature sieve tube is pictured as a mere skeleton of peptide chains holding a relatively large quantity of enmeshed water, it is conceivable that it offers little resistance to the intercellular flow of solution. Bateman observes that protein crystals should be regarded as bipolar coacervates, and that such para-crystalline suspensions containing rod- or leaf-shaped particles may contain water layers up to as much as 5000 A. in thickness.

As a final suggestion it should be emphasised that the peptide skeleton mentioned above should not be pictured as a rigid framework incapable of spacial adjustments. The chains are violently vibrated by thermal agitation and cushioned by associated water molecules as are the solute molecules passing along or through them. Consequently, just as seeds, in passing through a cleaner, are kept from clogging by the vibration of the screens, so sugars, amino acids and other assimilates moving through the mature sieve tubes should remain free of structural barriers.

Movement of the assimilate stream across phloem walls should be subject to similar considerations. Chemical analyses and X-ray studies have shown the structure of cellulose to be of a para-crystalline nature characterised by long chains of glucose residues bonded longitudinally by oxygen bridges and held laterally by hydrogen bonds.[11] Hydration results in lateral spreading of the chains with the intrusion of water molecules. Because these are also bonded by residual hydrogen valences, lateral spreading of the cellulose chains may be considerable, and mild chemical action may cause even greater hydration.

Most X-ray work on cellulose has been done on dry fibres. There is evidence [12] that sieve-tube walls are highly hydrated in their natural state and that their structure is less dense and less highly ordered than that of fibres. Measurements have shown that they shrink as much as 50 % upon drying and under polarised light their anisotropy is less marked than that of phloem fibres.

Using 50 % of the cross-sectional area of the phloem walls as the available channel, considering that the assimilate stream might contain 10 %, 15 % and 20 % solute, and assigning a possible 10 %, 20 % and 50 % of the total available pressure for forcing flow through the restricted stolon, values for the dimensions of capillary spaces required to accommodate transport into the potato tuber have been calculated.[8] Table I gives the results.

TABLE I

DIMENSIONS OF CAPILLARY SPACES REQUIRED TO ACCOMMODATE MOVEMENT OF THE ASSIMILATE STREAM THROUGH THE STOLON OF THE POTATO; CALCULATIONS BASED ON SUCROSE

Solute Conc.	Solute Conc.	Osmotic Pressure at 25° C	Dimensions of Capillary Spaces Distances between Parallel Planes		
			Pressure Utilised		
%	Molal	Atm.	10 %	20 %	50 %
10	0·33	8·5	660 A.	460 A.	290 A.
15	0·52	13·5	430	310	190
20	0·73	19·4	330	230	150

From these results it seems that spaces of the order of 150–450 A. would be required to accommodate flow. These calculations by a modification of Poiseuille's formula assume the walls of the capillary spaces to be rigid, as for instance the walls of a glass tube, and they assume stream-line flow.

A more detailed study of the constitution of cellulose proves that it is composed not only of crystallised regions, but also contains amorphous regions. Certain studies indicate that the consistency of cellulose is like that of a suspension of rod-like particles immersed in a viscous fluid. Stress tends to parallelise the rods, the degree depending upon the elongation produced. Highly swollen samples show this phenomenon to a marked degree and the relation of oriented rod structure to amorphous material may be measured in X-ray diagrams since the crystallised portions produce the sharp, intense interference spots while the amorphous parts produce the general background.[13] While the X-ray diagrams give an indication of the unit cell of anhydrous cellulose fibres the spacings of units in the amorphous portion are not given. The dimensions of the unit cell as given by Meyer and Misch (1937) are:

$$a = 8\cdot35 \text{ A.};\ b = 10\cdot3 \text{ A. (fibre period)};\ c = 7\cdot9 \text{ A.};\ \beta = 84^\circ.$$

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[11] Wise, *Wood Chemistry* (Reinhold, New York, 1944).

[12] Crafts, *Plant Physiol*, 1931, **6**, 1.

[13] Mark, in Wise's *Wood Chemistry* (Reinhold, New York, 1944).

The chains at rest in this structure have intermolecular spacings of only 2–3 A.

At first glance it might seem that the close spacing of the chains in cellulose must preclude the ready movement of molecules of the size of sucrose and amino acids through cell walls. On the other hand, it is well known that sucrose molecules rapidly traverse walls of living cells whenever plasmolysis with this material is carried out. And this is true of phloem walls because young sieve tubes may be readily plasmolysed and parenchyma cells of mature phloem rapidly respond to plasmolising solutions.

In seeking an answer to this question there appear several suggestions. First, hydration must result in a radical separation of the chain structure of the cellulose of phloem walls. Shrinking of phloem walls indicates this to be of an entirely different order of magnitude than the chemical hydration of cellulose by decomposition of cellulose derivatives (regeneration). Second, spacings in the amorphous portions of the cell wall may be much less regular than in the crystalline regions and may attain dimensions of the order of those indicated in Table I. Finally, phloem walls may be made up of a different type of cellulosic material than walls of other tissues. Attention is called to the nacré condition of the walls of protophloem elements. Walls of secondary phloem sieve tubes, though less strikingly specialised, are always thick and the end walls in particular are much less birefringent than are the walls of fibres. This is evidence for weakness of the primary bonding forces of this type of cellulose, and may in part account for the high state of hydration. It seems probable that the specialisation of the walls of phloem conductors is, like that of the protoplasm, designed to accommodate the rapid flow of assimilates in solution.

Conclusions

As previously mentioned, studies on the transport of viruses, dyes, hormones and growth regulators indicate a correlated movement of these indicators with foods in the phloem. Specialisation of the phloem conductors would seem to favour such movement. Plasmolysis tests prove that the protoplasm of the mature sieve tube is highly permeable. Cytologic studies show a loss of nucleus, a lowering of the retention of dyes, and a change from a fluid to a tough, fibrous consistency. Though far from complete, the evidence cited here from physico-chemical studies indicates that the degradation resulting from the above changes produces an open skeletal structure of peptide chains of high permeability. Specialisation of sieve-tube walls seems again to be in the direction of high permeability.

If we examine the two proposed mechanisms for explaining phloem transport, it seems that the specialisation mentioned would have little benefit for movement of a diffusional type ; in fact, the positive cytological evidence for protoplast degradation in the sieve element would seem to be detrimental to any postulated mechanism of activation dependent upon metabolic energy. And the specialisation of end walls would not help, for in diffusional movement, passage of assimilates would be attended by constant breaking of residual bonds as the molecules pass through the relatively static vacuolar water, and movement across end walls should add little to the total resistance. For convectional flow, on the other hand, movement through the vacuole would require only breaking of bonds along the periphery of each liquid column and flow through end walls would constitute a major item of resistance. Here the specialisation of the cytoplasm and cell-wall material certainly favours mass flow.

Specialisation for the accommodation of translocation of solutes in plants has undergone three essential stages. (1) Elongation of cells and streaming of protoplasm that facilitate diffusion. This occurs in mosses and certain algæ and in the mesophyll and border parenchyma of higher plants. (2) Increase in permeability of cytoplasm and walls of specialised phloem conductors. This occurs in the large algæ, mosses, lycopods, ferns and all higher plants. (3) Loss of protoplasm and perforation of the walls of specialised xylem elements found in tracheophytes occupying a terrestrial environment. In view of the extreme specialisation of the third type that is commonly recognised, the second as suggested here does not seem improbable.

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WATER MOVEMENT IN LEAVES

By F. J. Lewis

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Transpiration, the emission of water vapour from the open stomata on the leaf surface, may be considered to consist of two stages : (*a*) the emission of water vapour from the interior of the mesophyll cells into the air-space system between the cells, and (*b*) the passage of water vapour out between the guard cells of the stomata (when they are open) to the exterior.

In the long series of researches on transpiration during the last fifty years most attention has been paid to stage (*b*), and the behaviour of the stomata has usually been considered as governing the rate of transpiration, and little attention has been given to conditions at the surface of the mesophyll cells where the water vapour actually leaves the tissues of the plant. The emission of water vapour from the outer surface of the mesophyll has usually been assumed to be a process of evaporation in which no protoplasmic activity is concerned, and the surface of the wall stated to be moist or covered by a thin film of water.

It seemed desirable to investigate the properties of this surface in the light of these suggestions, or, in other words, to study transpiration without the epidermis and stomatal control.

The only means of doing this is to study the exit of water from the surface of the mesophyll without the epidermis. Two methods may be used, (*a*) cutting the epidermis so that there is a free passage from the air-space system to the external atmosphere, (*b*) getting rid of the epidermis altogether. It has been generally considered that slitting the epidermis is preferable as inflicting less injury to the leaf and this method was used by Francis Darwin early in the present century. Experiments conducted on these lines gave a rise of 10 % to 100 % in transpiration in light over that in darkness. These results were open to question as no account was taken for shock to the tissues due to injury. Similar experiments were carried out more recently.[1] These show only a transpiration rise of about 5 %, but in addition the experiments indicated that the rate of loss of water from the mesophyll was greatly affected by light, and that light of a certain intensity gave a much increased rate if supplied intermittently, and that 2000 flashes per minute were much more effective than continuous light of the same intensity. These experiments are interesting as attempts to study the conditions at the real seat of transpiration instead of at the external surface of the leaf. None of these experiments were directed to an examination of the conditions at, or the characters of the surface of, the walls of the mesophyll cells where the water vapour originates.

It seemed to be desirable to make some observations of these surfaces. This can only be done by eliminating the epidermis. Search for suitable leaves for experiment soon showed that some leaves could be stripped of the epidermis with great ease and without injury to the mesophyll cells lying below. Early experiments with *Ficus elastica* in Egypt gave good results but suggested that the age of the leaf and also its turgidity greatly affected the ease with which the epidermis could be removed. Other leaves proved to be better experimental material although all the earlier work was carried out with *Ficus*. *Hyoscyamus muticus* leaves proved to be excellent, and *Canna*, *Morus*, *Malva*, *Pancratium*, *Caryota*, *Ricinus* and many others have been used. Lately *Saxifraga sarmentosum* has been found to strip so easily that nearly the whole stomatal epidermis could be removed at one operation.

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[1] Henderson, *Ann. Botany*, 1926.

The stripping of the epidermis inflicts no deep-seated injury to the layer of mesophyll for the epidermis comes away easily and is clear from any torn-off mesophyll cells and the leaf shows no injury after 24 hours. The mesophyll layer consists of a loose tissue of irregularly rounded cells with a system of continuous air-spaces separating the cells from one another. The proportion of volume of air-space to cellular space differs in leaves of various ecological types, but frequently the air-space system occupies a greater volume than the cellular tissue. It follows that the actual area of the surface of the mesophyll cells abutting on the air-space may be very considerable.

The experimental method first employed consisted in cutting leaf strips parallel to the lateral veins, and for these first experiments the leaf of *Ficus elastica* was chosen. If such strips are suspended vertically with the lower edge in contact with water, no entry of water takes place into the capillary system between the mesophyll cells, and the same result is observed if the whole strip is immersed in water. It makes no difference whether this experiment is carried out in light or darkness, and all attempts to induce the entry of water into the air-spaces proved unsuccessful.

Experiments were made to determine the possibility of the entry of other liquids under similar conditions. Leaf strips suspended vertically over benzene, chloroform, ether, petroleum ether, acetone, essential oils, olive oil and pure medicinal paraffin showed that with all these liquids entry takes place at once, the liquid rushing with great velocity into the capillary spaces between the mesophyll cells. With benzene, chloroform, ether and petroleum ether a vertical rise of 2 cm. may be obtained in less than 60 sec., and the rise goes on at a progressive rate until the inflow reaches the upper edge of the strip. The entry of essential oils, olive oil and paraffin is somewhat slower, but even with paraffin a rise of 5 mm. can be observed to occur in approximately 5 min.

Direct microscopic observations of the mesophyll layer in relation to the flow of liquids seemed to be desirable and were carried out in the following manner. The leaf of *Ficus elastica* can easily be torn transversely by suitable manipulation so that considerable areas of uninjured mesophyll are exposed, for the lower hypodermis readily splits away from the upper portion of the leaf. If the operation be carried out rapidly, no injury to the cells takes place except to the individual cell-ends next to the hypodermis. A strip of up to 2 cm. in length and breadth can then be examined under a magnification of 100 or more and an excellent view of the space system and the small lateral veins be maintained.

A drop of water placed on this surface remains suspended like a lens on the summits of the mesophyll cells and shows no disposition to spread over their surface into the capillary system. When a drop of the organic liquids mentioned earlier is used in the same way, instant entry into the intercellular spaces occurs. All these liquids, except medicinal paraffin, have the disadvantage of being toxic and rapidly killing the cells with which they come into contact. While the phenomena to be described do not vary essentially whatever liquid is used, the microscopic observations relate only to the use of pure paraffin. The use of this hydrocarbon further had the advantage of its behaviour being easily followed, while the entry of the other liquids is so rapid that it cannot be followed with the eye.

When a drop of paraffin is placed at one end of the leaf strip with the mesophyll surface exposed, the oil immediately penetrates the capillary system. Two advancing fronts can be observed. From the edge of the drop, a stream comes out which cascades down into the air-space system and this is followed by the main wave. The two waves pass along the strip about 1 mm. apart, and the oil thus travels the length of the exposed mesophyll. When a drop of water is placed about the middle of the strip and oil added at one end, the oil travels along until it comes to the water, and the initial oil-wave trickles into the air-spaces below the water lens and continues its path on the further side.

Experiments with Water-oil Mixtures.—If a small quantity of water is shaken up with a much larger amount of paraffin so that the water droplets are of the order of about 0·001 mm. diam. and the mixture placed at one end of the strip of exposed mesophyll, the oil enters the air-space system carrying some water droplets floating in it. It sometimes happens that a water droplet comes into contact with one of the fine veins bared by accidental removal of a cell of the bundle sheath traversing the mesophyll. When this happens, the water droplet appears to adhere to the surface of the vein, often sends out an arm or narrow outflow on one or two sides, loses its spherical shape, becomes flattened, diminishes in size, and finally disappears, being absorbed into the vein. When such a water droplet is swept against a mesophyll cell wall by the current of oil, no change takes place and, in the absence of a current of oil sweeping it away, remains unchanged in position. When an emulsion of a small quantity of benzene in water is used, the behaviour of the mesophyll can be observed macroscopically. If leaf strips be placed in such an emulsion and the containing tube slowly agitated, the ends of the leaf strips become infiltrated with benzene and the turbidity of the water-benzene almost disappears owing to the absorption of the larger droplets of benzene into the mesophyll air-spaces. The same events are shown when paraffin is used instead of benzene.

When a leaf strip with the mesophyll exposed is prepared and quickly placed on a slide under the microscope and covered with a cover-glass, moisture immediately collects on the under surface of the glass. It forms at first a system of microscopic polygonal strands of water, giving a minute shagreen aspect to the glass when observed with a magnification of 100. After a few minutes the strands coalesce. If water is now run in under the cover-glass, it immediately penetrates between the wet cover-glass and the mesophyll, but does not flow down into the air-spaces of the mesophyll. If a drop of paraffin is placed in contact with the edge of the leaf, it quickly passes into the air-spaces and is bounded above by the water film still adhering to the glass which, owing to slight inequalities of the surface of the mesophyll, is distant 0·01 to 0·001 mm. From these observations it appears that while the mesophyll is passing off water vapour rapidly into the air, and this is condensed on the surface of the cover-glass, the cell walls from which the vapour proceeds cannot be wetted.

Infiltration of the Whole Leaf with Water and Paraffin.—Leaves infiltrated with water by a pressure gradient were found on exposure to bright sunlight to clear the mesophyll of liquid in a period of about two hours. Observed by transmitted sunlight under slight magnification (× 10), the retreat of the water appears to be a markedly discontinuous process, the water receding suddenly from areas several millimetres broad and then halting for a time.

Infiltration of the mesophyll air-spaces takes place with paraffin without a pressure gradient. If the petiole of a whole leaf is placed in paraffin, the oil passes up through the intercellular spaces of the petiole and enters the air-spaces of the leaf. This occurs more rapidly if the leaf is cut in half transversely to avoid air-locks in the mesophyll. It can be observed that the oil does not enter the vascular bundles of the petiole: its passage is solely through the intercellular spaces.

Observations were made on the pressure infiltration of acid and basic dyes in aqueous solution. With basic dyes such as Janus green, Methylene Blue, the whole of the dyestuff in solution is retained and adsorbed on the surface of the mesophyll cells at the point of entry, while the uncoloured water passes on and fills the interspaces of the mesophyll. The usual method adopted was to cut the leaf in half transversely, connect the cut petiole with a vacuum pump and place the leaf in the dye solution. Acid dyes when introduced into the air-spaces by the same means show no adsorption on the cell walls.

Numerous experiments have been carried out with the object of rendering the cell walls wettable by water. It was found that if one of the fatty acids such as sodium taurocholate in slight bulk concentration in water be placed as a drop on the exposed mesophyll, it begins to spread and after an interval of 1 or 2 min. the bubbles of air in the interspaces below are displaced and the liquid spreads out and fills the interspaces. The action is exactly similar to that observed with paraffin, but the rate is very much slower. Leaf strips with the lower edge in contact with water containing a minute proportion of sodium taurocholate (between 1/100,000 and 1/200,000) showed a rise into the mesophyll spaces, and the infiltration proceeded up the strip in the same manner as paraffin, but the action was arrested about 5 mm. from the point of entry where a brown band of discoloration appeared.

The action of the liquid on the exposed mesophyll is sensitive to *p*H values and it was found that the reaction takes place readily at *p*H 6·2, and very slowly if at all on the alkaline side. These observations show: (1) that the outer surface of the mesophyll cell walls from which all the water of transpiration is given off is highly hydrophobic, (2) that they are quickly covered by a liquid hydrocarbon, (3) that on pressure infiltration with water, the liquid in the air-spaces is quickly cleared when the leaf is placed in strong sunlight and there is no adhesion to the surface by water, (4) that the wall surface shows strong adsorption with basic dyes in solution but no adsorption to acid dyes, (5) that the hydrophobic nature of the surface of the wall is destroyed by traces of sodium taurocholate in solution.

NOTE ADDED IN PROOF:

The observations recorded raise questions regarding:—

(*a*) how the water leaves the cells of the mesophyll;
(*b*) how the vapour is given off from the cell wall;
(*c*) the factors which govern the changes in the rate of transpiration from the mesophyll cells.

Many observations have been made by microscopic examination which suggest that there may be a secretion of water from the cells. This is supported by the fact that a layer of water can form on the exposed mesophyll surface when the surface is covered with a thin film of oil if in strong transmitted light. If a leaf with exposed mesophyll is immersed in oil and viewed by direct transmitted sunlight, water globules can be seen to form in the air spaces of the mesophyll.

By direct visual observations it can be seen that the amount of water deposited on a cover glass suspended 1 mm. above the exposed mesophyll is greatly increased on exposure to direct sunlight.

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ADHESION OF WATER TO THE EXTERNAL SURFACES OF LEAVES

BY G. E. FOGG

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Studies of the adhesion of water to its external surface may be of considerable value in revealing some of the less obvious but nevertheless physiologically important features of plant epidermis. As yet, the method has scarcely been used.

The adhesion between a solid surface and a liquid applied to it may be conveniently measured in terms of contact angle. In the case of plant epidermis, advancing contact angles are easily determined from profiles of drops resting on horizontal leaf surfaces. They may be measured directly but, because leaf surfaces are generally irregular, it is better to derive a value by calculation from the characteristics of the drop outline, since this gives a mean value for the whole periphery of contact rather than that at a single point. Details of suitable methods are given elsewhere.[1] Contact angles may vary considerably even on apparently comparable leaves so that means of several determinations must be used for comparisons. The results presented in Table I are mean values ($\bar{\theta}_D$) with their standard deviations each derived from 9 to 12 determinations of the advancing contact angle of clean water on the upper surfaces of samples of from 4 to 6 healthy mature leaves selected at random.

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[1] Fogg, *Proc. Roy. Soc.* B, 1947, 134, 503.

TABLE I

$\bar{\theta}_D$ for Water on (*a*) Fresh Leaves, (*b*) Similar Leaves after Extraction with Benzene (Ether in the Case of *Sinapis*), (*c*) the Benzene-Soluble Material from (*b*) Deposited from Chloroform on Clean Glass

Species	Nature of Surface	*a*	*b*	*c*
Nymphaea sp.	nearly plane	67·8 ± 1·60	85·5 ± 1·02	48·1 ± 2·48
Prunus laurocerasus	„ „	75·5 ± 2·08	81·3 ± 1·06	87·6 ± 2·05
Sinapis arvensis	corrugated	96·0 ± 4·73	29·4 ± 8·28	—
Triticum vulgare	„	141·3 ± 2·04	122·0 ± 1·82	104·8 ± 0·53

The magnitude of the observed contact angle of a given liquid is determined by two characteristics of the solid on which it rests; i.e., the nature of the chemical groups exposed in the surface and its roughness. Where the effect of the latter can be assessed or neglected, the degree of adhesion of water to its surface gives information regarding the nature of the most superficial layers of the epidermis. The composition and structure of these layers have only been investigated for a few especially favourable species and the generalisations which follow must be regarded as tentative. Judging from micro-chemical tests, the most external layer visible, the cuticle, is composed largely of cutin, a substance insoluble in lipoid solvents, yielding various oxy-fatty acids on hydrolysis.[2] Optical[3] and electron microscope studies[4] show that it is homogeneous and isotropic, with the long-chain molecules orientated at random. The cuticle, together with the cutinised layers below it, also contains components of a waxy nature,[2] comprising long-chain paraffins, ketones and alcohols,[5] and small amounts of water-soluble substances, probably glucosides of the saponin type.[2] Exact measurements do not seem to have been made, but cutin appears to be appreciably permeable to water, and since it contains polar groups it is to be expected that its adhesion for water is intermediate in magnitude between that of waxes and of cellulose. This is borne out by the values for the contact angle of water on the surface of epidermis extracted with wax solvents, which are less than those for water on wax surfaces providing that roughness is not a complicating factor (cp. Table I). However, the presence of small amounts of other substances at or near the surface of the cutin will considerably modify its adhesion for water. That such substances are generally present is shown by the marked alterations in the contact angle of water on leaves, produced by extraction of the latter in the cold for a short period by solvents such as ether or benzene. Leaves are killed by such treatment, but it has been shown that death itself does not involve appreciable alteration in the surface properties of leaves[1] such as might be expected if relatively rapid adjustment of tissue tensions with corresponding changes in epidermal corrugation occurred. In the case of terrestrial plants such as *Triticum* and *Prunus*, the extracts contain small quantities of substances, probably similar to the wax components that have been isolated from epidermis,[5] against which water has a high contact angle (cp. Table I). It cannot be said whether these are present throughout the cutin matrix or only as a film on its surface, or whether, if several substances are present, they are distributed in the same proportions in different parts. In some species there is a visible wax deposit on the surface of the cuticle. No such deposit is detectable microscopically in *Triticum* or *Prunus*, but a layer only a few molecules thick would be effective in decreasing the adhesion of the epidermis for water. Such films, if present, would also have a considerable effect on the permeability of the epidermis to water.[6] In the cutinised layers, double refraction shows the wax molecules to be orientated at right-angles to the plane of the epidermis [3] and it seems probable that this would also be the case in films on the external surfaces of aerial leaves generally. The paraffin chains are presumably directed outwards as at the surface of similar substances solidified from a melt.[7]

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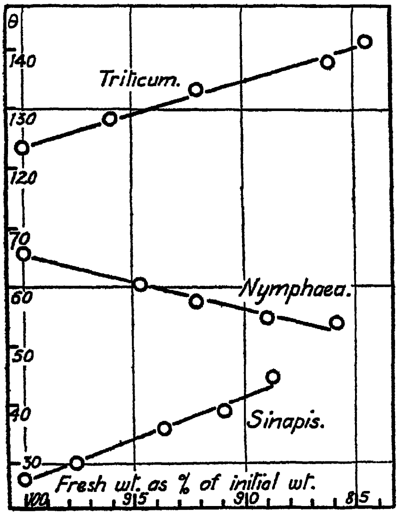
[2] Legg and Wheeler, *J. Chem. Soc.*, 1925, **127**, 1412.

[3] Meyer, *Protoplasma*, 1938, **29**, 552.

[4] Watson, *Can. J. Res.*, 1943, **21**, 89

[5] Chibnall, Piper, Pollard, Smith and Williams, *Biochem. J.*, 1931, **25**, 2095.



In *Nymphaea*, an aquatic plant with floating leaves, the epidermal surface becomes less hydrophilic after benzene or ether extraction and the extracts are found to contain material insoluble in water but against which water has a low contact angle (cp. Table). The presence of such hydrophilic substances in the cuticle may be related to the fact that development of the leaves takes place under water. Possibly the molecules are orientated at the surface with the polar groups outwards and the non-polar portions associated with those of the cutin. The contact angle on intact *Nymphaea* epidermis is rather higher than that on the benzene-soluble material; this difference is not accounted for by corrugation of the epidermis so it appears that the more hydrophobic constituents of the cuticle left after extraction may not be completely masked by the hydrophilic components readily soluble in benzene.

Leaf surfaces are rarely plane and in the case of some plants the contact angle of water on them is considerably modified by their corrugation. Where a solid surface beneath a drop is completely in contact with the liquid the observed contact angle (θ_D) differs from the true contact angle on a plane surface of the same composition (θ) according to the relation

$$\cos \theta_D = f \cos \theta \quad . \quad . \quad . \quad . \quad (1)$$

where f is the roughness factor (actual surface/geometric surface) [8] [9]. θ_D is therefore greater or less than θ according to whether the latter is greater or less than 90°. This equation may be applied in the cases of plants such as *Nymphaea*, the leaves of which can be completely covered with water; however, no methods for the determination of θ and f for leaf surfaces have yet been devised so its usefulness is limited.

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[6] Alexander, Kitchener and Briscoe, *Trans. Faraday Soc.*, 1944, **40**, 10.
[7] Adam and Jessop, *J. Chem. Soc.*, 1925, **127**, 1863.
[8] Wenzel, *Ind. Eng. Chem.*, 1936, **28**, 988.
[9] Cassie and Baxter, *Trans. Faraday Soc.*, 1944, **40**, 546.

The surfaces of most aerial leaves cannot be covered with water completely, air films being retained beneath the drops. In such cases, observed contact angles are greater than true contact angles, and the expression

$$\cos \theta_D = f_1 \cos \theta - f_2 \quad . \quad . \quad . \quad . \quad (2)$$

seems to be applicable, f_1 being the area of solid-liquid interface and f_2 the area of air-liquid interface per unit superficial area of contact.[9] [10] Leaf surfaces differ in the following respects from the simple porous surfaces for which this relation has been experimentally verified.

(1) They are not necessarily truly porous, air being trapped beneath a water drop and not always in free communication with the atmosphere. If the upper surface of a leaf such as one from *Sinapis arvensis* were porous, the whole area beneath a drop would be in contact with the water, since the corrugations are shallow and θ is small. In actual fact, considerable air films are retained and this being so the water-air interfaces beneath the drop must be curved and not plane as they would be if the surface were porous.

(2) The corrugations are rarely of the simple cylindrical form studied in physical investigations. The considerable variations in form found in different species produce different degrees of wetting, thus acute projections give a high value for f_2 and a correspondingly high value for θ_D, whereas obtuse projections will have the opposite effect.

(3) The corrugations of a leaf surface may be on different scales and superimposed. For example, the upper surface of a *Triticum* leaf is corrugated longitudinally, each ridge being approximately semi-cylindrical and about 0·25 mm. diam., and further roughened by each epidermal cell projecting as an oblong bulge approximately 0·05 × 0·015 mm. and 0·004 mm. high. In some species there may be wrinkling of the cuticle on a still smaller scale.[11] In such cases, contact between leaf surface and water may be complete with respect to the smaller corrugations and so f_1 in eqn. (2) will be larger than the geometrical area of liquid-solid contact and θ_D will be increased or decreased according as to whether θ is greater or less than 90°.

These complications do not affect the validity of eqn. (2) for the particular systems being discussed but render calculations involving the form and magnitude of the surface corrugations very difficult. The expression may, however, be used for determining values for f_1 and f_2 from known contact angles; thus, if it is assumed that θ is equal to the angle of contact on the extracted wax, as it probably is for *Triticum*, and that $f_1 + f_2 \simeq 1$, then using the values given in Table I, it is found that $f_1 = 0{\cdot}3$ and $f_2 = 0{\cdot}7$. It would be desirable to check such values, which are of importance in studies on the penetration of substances into leaves from solutions sprayed on to foliage,[1] [12] against those determined by some other method, but this has not yet been done.

The magnitude of the contact angle of water on a leaf surface has been found to vary with the position of the leaf on the plant.[1] Such variation is very likely due to differences in the degree of corrugation of the epidermal surface but the point has not yet received experimental investigation. In addition, in certain species of plant at least, there is considerable fluctuation of the contact angle of water on similar samples of leaves within short periods of time. In plants of *Sinapis* growing under natural conditions, a diurnal variation through a range which may be as much as 30° has been observed. Contact angles also show characteristic changes during wilting of a leaf.[1] [13]

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[10] Cassie and Baxter, *Nature*, 1945, **155**, 21.

[11] Martens, *Protoplasma*, 1934, **20**, 483.

[12] Fogg, *Ann. Appl. Biol.*, 1948 (in press).

[13] Fogg, *Nature*, 1944, **154**, 515.

There is qualitative evidence that both types of variation are due to changes in the degree of corrugation of the epidermis resulting from changes in the water content of the leaf tissues.[1] At present it is only possible to give empirical relations between the water content of a leaf and the apparent contact angle of water on its external surface. Data (presented more fully elsewhere [1 13]) for leaves of various species losing water slowly are given in the figure and show that, in the earlier stages of wilting at least, there is an approximately linear relation between the two. In the case of *Nymphaea* the increase in corrugation attendant upon loss of water from the leaf results in a decrease in apparent contact angle, as would be expected from eqn. (1), whereas in the cases of species in which air films are retained beneath drops there is an increase in apparent contact angle. As is to be expected from eqn. (2), if changes in f_1 and f_2 are of the same orders per unit water-loss in different species, the rate of change of θ_D during wilting is smaller at high values (*Triticum*) than at low values (*Sinapis*). If leaves are wilted rapidly the changes in contact angle may be less regular and give evidence of differential variations in tissue tensions. Thus on *Sinapis* leaves an initial fall in contact angle indicates that the surface becomes smoother as the superficial tissues lose water more rapidly and become stretched on the still turgid tissues beneath. Later, as the latter begin to dry out, the contact angle increases.[1]

Summary

The advancing contact angle of water on the exterior surface of a leaf provides a convenient measure of the adhesion between the two. The true contact angle on the surface of the cuticle appears to be largely determined by films of hydrophobic or hydrophilic substances although the adhesion of water to its principal component, cutin, is of an intermediate magnitude. Observed contact angles differ from true contact angles according to the extent of corrugation of a leaf surface. Expressions connecting the two for rough and porous surfaces are respectively applicable in the cases where the leaf surface is completely covered by water and where air films are retained beneath the drops. The extent of corrugation of a leaf surface alters with the water relations of the tissues beneath, observed contact angles showing corresponding changes.

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GENERAL DISCUSSION

Dr. R. D. Preston (*Leeds*) said: In answer to a question by Dr. Crisp, unfortunately, in intact sieve tubes the cytoplasm is in close contact with the walls, so that the question is whether the surface of a liquid in contact with a surface of the consistency of a cellulose layer can move sufficiently rapidly.

Dr. D. J. Crisp (*Cambridge*) said: The possibility has been raised that interfacial transport may account for rapid movements of metabolites in living tissues, notably in the sieve tubes of phloem.

A distinction must be made between true interfacial diffusion under the influence of Brownian forces and interfacial flow. The former may occur at any kind of interface and is independent of conditions outside the interface; but it is probably a slow process, comparable to diffusion in bulk. Interfacial flow, however, may lead to rapid translocation of material in favourable circumstances. In this process the whole interface moves under a surface pressure gradient carrying the bounding layers of liquid and setting up convection currents.[1, 2]

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[1] Crisp, *Trans. Faraday Soc.*, 1946, **42**, 619.

[2] Sollner, *Kolloid-Z.*, 1933, **62**, 31.

It seems unlikely, however, that the right conditions for this process exist in the sieve tubes of the phloem. It is necessary:

(*a*) that the interface should be mobile. An interface involving a solid or very viscous surface cannot be the seat of rapid interfacial flow as slip does not occur between the interface and the boundary phases.[1]

(*b*) Similarly, the fluids bounding the interface must be free to move. A solid boundary very close though not touching the interface will restrict movement owing to the very great drag of the thin film of liquid intervening.

(*c*) One at least of the materials being transported must be able to adsorb at the interface and to desorb at the region of low concentration, thus causing a significant change of interfacial tension.

As the interface between the cell wall and protoplasm is solid-liquid this is eliminated under (*a*). The interface between the central vacuole and the protoplasm is probably of very low interfacial tension,[3] and therefore adsorption involving a considerable further lowering of tension would be unlikely.

Prof. N. K. Adam (*Southampton*) said: I doubt whether transport along a *solid* surface can be rapid enough to account for the movement in plants. Spreading on a clean surface of *liquid* water can proceed at a rate of some 20 cm./sec., and can no doubt transport material at the required rate. In this spreading, the molecules of the underlying liquid move along the surface with the spreading substance, to which they are attached. The motion of a spreading substance is much more rapid than the diffusion of a dissolved substance through bulk liquid, since in bulk diffusion there are continual collisions driving the molecules backwards as well as forwards; but in spreading, once a molecule has been drawn forward by an attached underlying molecule of liquid, it cannot return, since its former place on the surface is taken by another spreading molecule.

The molecules on solid surfaces are not mobile, so that this mechanism is not available. Volmer's measurements[4] on the spreading of benzophenone on glass showed perceptible, but very slow transport of adsorbed molecules. Some mobility in adsorbed films on solid surfaces undoubtedly exists, but the rather scanty quantitative measurements of its speed indicate that it is several orders of magnitude slower than spreading on liquid surfaces.

Dr. R. K. Schofield (*Harpenden*) said: Under natural conditions the transpiration of a mass of vegetation is largely controlled by the solar radiation incident upon the area of ground that it covers, since the heat of vaporisation is drawn from the radiant energy. Thus, in practice, it is the energy supply and not the total leave surface that mainly controls transpiration.

Prof. T. H. van den Honert (*Leiden*) said: In 1932, I suggested a mechanism of transport of organic material, due to spreading along a liquid surface and caused by surface-active forces, in the same way as proposed by Dr. Crisp. I devised a simple apparatus to demonstrate such a mechanism.[5] It consisted essentially of two small flasks connected by a 1 m.-long horizontal glass tube. A rapid spreading of sodium oleate through this tube along an interface between ether and water was demonstrated by means of an indicator added to the water. The transport rate was roughly 68,000 times that accounted for by mere diffusion. I presume that it is possible that the interface between protoplasm and vacuole could be the seat of a similar transport.

Dr. R. D. Preston (*Leeds*) said: It should be noted that the figures calculated for the dimensions of capillary spaces are quite artificial and should not be compared, for instance, with the 100 A. spaces discussed by Schofield. As regards the statements made by Crafts concerning wall structure, certain points need clarifying. Crafts clearly implies that the dimensions of the accepted unit cell of cellulose applies only to anhydrous fibres, and that hydration "must result in a radical separation of the chain structure of the cellulose of phloem walls," and then, quoting the known high shrinkage in phloem walls, suggests that these walls might be made up of a different type of cellulose. It should be stressed that hydration does not separate the chains of cellulose inside a micelle, for water does not penetrate there; nor is it necessary to imply micellar penetration of water or to invoke a different crystalline structure to the cellulose to explain the high shrinkage. Cases are known where intermicellar shrinkage and swelling are even higher than here, dependent entirely on the relative amount of non-crystalline cellulose and the amount and quality of the incrusting substances (Preston and Duckworth).

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[3] Harvey and Danielli, *Biol. Rev.*, 1938, **13**, 319.

[4] *Z. physik. Chem.*, 1926, **119**, 46.

[5] van den Honert: *Proc. Kon. Akad. Wet. Amsterdam*, 1932, **35**, 1104.

Incidentally, it should be noted that the intermolecular spacings in the non-crystalline fraction *must be* (not "may be") less regular than in the crystalline fraction. As regards the crystalline structure of sieve tube walls, I am not aware of any decisive evidence on this point; but I have X-ray photographs of the whole phloem in which the cellulose appears quite normal. Finally, the birefringence of walls cannot be used as evidence concerning the primary bonding forces; the low birefringence can be due to one or more of a large number of factors—the orientation factor, high angular dispersion, low crystalline/non-crystalline ratio, low total cellulose content, etc. On the whole it seems rather certain that in phloem walls the "intermicellar" spaces may be unusually large, but whether they can be treated as water-filled spaces in the sense demanded by Crafts seems rather uncertain.

I do not know of any evidence relating the movement of sugars and amino acids, but there is the clear case discussed some years ago by Palmquist in which he demonstrated simultaneous opposite movement, in a leaf stalk, of fluorescein and sugar. It is not, of course, certain that the two substances were moving in the same sieve tube or even in the same phloem strand, but there seems no reason to suppose that any one sieve tube is concerned solely with downward or any one with upward movement.

Mr. S. E. Arney (*Southampton*) said: The fluorescence of fluorescein in infra-red radiation depends on the *p*H of the tissue, and the xylem is often too acid to allow any fluorescence, although relatively greater quantities may have travelled down in the xylem than in the phloem in these cases. This was demonstrated by Rhodes,[6] who also showed that the transport of fluorescein in the phloem was often slow, or almost non-existent in certain cases, while travel in the xylem was rapid. The contradictory results obtained with fluorescein, together with the fact that it is not a normal constituent of the tissues, makes it necessary to regard conclusions about the nature of translocation based on experiments with fluorescein with considerable reserve.[7]

The simultaneous movement of carbohydrate in one direction in the phloem, and of nitrogenous materials in the opposite direction in the phloem also, has been shown to be very probable, as a result of the work of Phillis and Mason on the cotton plant.[8] But whereas the movement of nitrogenous substances was only large enough to be statistically significant in one of the two identical experiments, the movement of carbohydrates in the opposite direction was only large enough to be statistically significant in the other experiment of the pair. Judged by the most rigorous standards, therefore, the phenomenon of simultaneous transport in opposite directions in the phloem can still be regarded as not proven.

Dr. R. D. Preston (*Leeds*) said: I was at Leeds myself at the time this work of Rhodes was carried out, and I think I should say that, though a striking demonstration, this work did not prove that fluorescein was *travelling* down the xylem. Hüber and others, in fact, claimed subsequently that fluorescein could be detected in phloem when its presence in the xylem could not be demonstrated even after the necessary adjustment of *p*H.

Prof. T. H. van den Honert (*Leiden*) said: The interesting properties of the boundaries of the intercellular spaces, as demonstrated in Dr. Lewis' experiments, are suggested by him to be of influence on the transpiration rate. Although I cannot disprove it, this does not seem very probable to me. For, as argued in my own paper, it would imply that in the cell-walls lining the intercellular spaces there would be a resistance against water movement, greater than in the whole rest of the plant, as if these cell-walls were covered by a cuticle.

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[6] *Proc. Leeds Phil. Soc.*, 1937, 389.
[7] *Proc. Leeds Phil. Soc.*, 1946, **1**, 343.
[8] *Ann. Bot.*, **50**, 141.

I like to visualise the non-wettability of these cell-walls from another point of view. For gaseous exchange, it is essential that the intercellular spaces be filled with a gas and not with water. It reminds one of Krogh's calculations,[9] who demonstrated that in the tracheæ of insects mere diffusion provides an adequate means of transport of oxygen, if only the tracheæ are filled with a gas. If filled with water, the oxygen diffusion would be 300,000 times as slow.

In the same way, the diffusion rate of carbon dioxide into the leaf would be completely insufficient if the intercellular spaces were filled with water.

Dr. R. K. Schofield (*Harpenden*) said : The curve of Fig. 2 in Bennet-Clark's paper is challenging but it is not clear how it is to be explained with the aid of electro-endosmosis. If the protoplasm itself occupied an appreciable volume, its swelling might have explained the initial increase in volume due to the washing-out of KCl while its shrinkage might similarly have accounted for the sharp decrease in volume on re-immersion in KCl. While this explanation appears to be untenable in view of the small volume of the protoplasm, it certainly appears from the form of the curve that there are two parts of the vacuole system, one of which reacts more quickly than the other.

[9] Krogh, *The Comparative Physiology of Respiratory Mechanisms.* (Philadelphia, 1941)

III. ZOOLOGICAL ASPECTS

WATER-PROTECTING PROPERTIES OF CUTICLES

Introductory Paper

By J. H. Schulman

Received 10*th March*, 1948

Before a physical chemist can be of use in investigations on living or biological systems, it is essential for the physiologist and histologist to give a description of the system and, where possible, some of the chemistry of the substances which are involved. This has now been done for the insect cuticle, and Wigglesworth, Hurst, and Thorpe and Crisp give a generalised picture of certain insect cuticles and treat two aspects of the function of cuticle respectively :

(1) permeability of the cuticle to water vapour or water,

(2) adherence of gases to the cuticle surface in the presence of water.

The first subject deals more with the chemistry or physical chemistry of possible compounds which may influence the retention or uptake of water vapour by the insect ; the second deals chiefly with the physics of the system responsible for the construction of elementary gills for the insects' respiration.

The problems very briefly present themselves into : (*a*) what are the molecular forces involved in preventing water vapour from migrating through a membrane, living or artificial, and (*b*) what are the molecular forces involved in preventing bulk water from migrating through a membrane. It is interesting, from the point of view of the surface chemist, that the first problem deals with the characteristics of the polar group or groups of an amphipathic molecule, and the second with the CH_3 group of the molecule.

Wigglesworth and his collaborators state that the insect cuticle consists of superimposed layers composed of lipoid, tanned lipo-protein, tanned protein and chitin, and that pore canals penetrate these systems at right angles to the laminations of the endocuticle. These canals do not reach quite to the surface of the cuticle, but are covered by a very thin layer, 0·2–0·4μ thick, of a cement-protected wax. The whole system, up to and including the cement, is metabolically interconnected.

Wax Layer Theory of Water Retention

Wigglesworth, Beament, Slifer and Lees focus their attention on the properties, chemistry and physical chemistry, of this wax. From analogies with artificial systems which have been impregnated with these compounds, they suggest a straightforward physico-chemical mechanism for the retention of water by the insect cuticle. Their evidence is based chiefly on the following facts: the breakdown of water retention is caused by the removal by solvents of loosely bound lipoids; abrasion of the surface of the cuticle by alumina; and the raising of the temperature above the melting-point of the wax. Against this theory, e.g., the importance of a wax layer in the mechanism of water retention by the insect cuticle, seem to be the following facts.

The insect cuticle can control both the water vapour absorption and desorption as shown by the work of Lees, so the mechanism must be of a reversible nature. Lees considers the energetics of the adsorption of the water vapour against a concentration gradient and distinguishes between passive retention of the water vapour by an inert wax film and active secretion of water vapour by the live insect cuticle. Hurst emphasises the reversible and asymmetrical behaviour of the insect cuticle to the transport of water vapour by showing that the rates of evaporation of water differ some twenty times by placing an insect cuticle on water, water-endocuticle—epicuticle-air (normal), water-epicuticle—endocuticle-air (inverted). The unimpeded evaporation of water by the inverted cuticle can be inhibited by the addition of lecithin and very markedly so by the addition of cephalin to the insect cuticle. Slifer further shows that no measurable difference can be found in the nature or quantity of wax on grasshopper eggs during diapause, where complete water retention is observed, to cold broken diapause or hatching periods where the egg shells are permeable to water vapour. On the other hand, removal of the wax layer by solvents during diapause caused immediate desiccation of the egg.

Hurst shows experimentally that the interpretation of the abrasive action of dusts to produce water permeability of the insect cuticle is open to criticism. He suggests that only dry dusts are active, irrespective of their abrasive action, as *dry* dusts can remove labile lipoids from the insect cuticle, whereas *wet* dusts cannot adsorb lipoid, and are therefore inactive. The fact that the cuticle will only become permeable to water vapour through the action of dry dust is also shown by Hurst.

It would appear that all workers in this field agree that small quantities of lipoids play an important part in the control of water-balance in insects, but Hurst, chiefly, is not in agreement with either the proposed histology or physiology of the insect cuticle, as proposed by Wigglesworth and collaborators. It is very interesting to note that the latter school use the work of Sebba and Briscoe [1] to explain the phenomenon. This shows that a monolayer of a long-chain alcohol (C_{22}) and, less efficiently, long-chain acids when in a molecular packing which prevents water molecules from penetrating between the polar groups of the long-chain compounds can reduce the rate of evaporation of water to within 2 % of its normal value. This effect by one condensed (orientated) monolayer is much greater than that of an oil layer on water, of the thickness 0·2μ, which has been considered the order of thickness of the wax layers on insects and insect eggs.

It is important that, in order for this mechanism to function, there should be a free water interface on which the condensed monolayer can form. There is no evidence that a lipoid monolayer adsorbed onto a solid structure can prevent water evaporation. Further, it can be shown that continuous lipoid monolayers, or multilayers, cannot span micro-holes or spaces unless those holes are filled with water.[2] It may be mentioned here that the melting-point of lipoids in the form of monolayers does not necessarily correspond to the bulk crystal melting-point, but is usually lower.[3] Dervichian has shown that for several long-chain esters the two-dimensional melting-point corresponds to a vitreous state of the compound. The vitreous forms spread both spontaneously and rapidly on water, whereas the crystalline forms spread very slowly. It is difficult to explain all the facts, such as the *asymmetrical* behaviour of the cuticle to water-vapour retention, and the lateral diffusion in the epicuticle, as demonstrated by Hurst by means of a straightforward monolayer or multilayer structure on the Sebba and Briscoe principle. To meet these facts, Hurst has brought the following theory, and adapted the Sebba and Briscoe concept in a somewhat different manner.

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[1] Sebba and Briscoe, *J. Chem. Soc.* 1940, 106.

Lipo-protein Lamellar Organisation of the Epicuticle in the Form of a Porous Valve System

To overcome the difficulty of explaining the asymmetrical behaviour of the cuticle by the wax layer concept, Hurst suggests that the structure of the epicuticle consists of a laminated lipo-protein structure analogous to that of a nerve sheath proposed by Schmidt and Bear from their X-ray studies. This laminated multilayer structure, placed parallel to the surface of the cuticle, is held in position by a network of vertically arranged pores or fibriles. Hurst considers that water can swell the laminar-arranged multi-monolayers similar to the concept of the swollen soap micelles as suggested by the X-ray study of concentrated soap solutions.[4] Further, when swollen with water, emulsions of lecithin and cephalin can penetrate into the laminæ and enable these lipoids to orientate at the lipo-protein water interface.

Two important considerations can be taken into account: (1) there is now a system in existence which enables a layer of lipoid molecules to orientate themselves at a *water* interface and thus on compression can prevent water from evaporating on the Sebba and Briscoe principle; (2) the water coming from the endocuticle to the epicuticle can swell the porous laminar structure restrained between the fibrillar network by *lateral* diffusion. This swelling of the laminæ by water and shrinking of the network by the presence of air on the surface can present a mechanism for preventing the water from penetrating through the cuticle in the direction water-endocuticle—epicuticle-air. If water now replaces air on the surface of the cuticle, the restraining action of the fibrillar network is released, and water can flow through the cuticle in the direction water-epicuticle—endocuticle-air, thus explaining the asymmetrical behaviour of the cuticle. Hurst supports his histology by showing that catechol stains the epicuticle by a *lateral* diffusion in the laminæ. The oxidase present in the proteins in between the laminæ causes the reddening of the catechol solution *in situ*. Further, if alcohols replace the air on the above system, they act like air as a dehydrating media, but if hydrocarbons replace air, they remove the water-protecting lipoids, and thus leave the cuticle in a condition in which it can no longer restrict the flow of water. If, therefore, a dehydrating alcohol is now added to the hydrocarbon, water can be rapidly withdrawn from the insect through the cuticle, since the combination of hydrocarbon and alcohol is a good de-fatting agent, removing the lipoids both from between the epicuticle laminæ and from the surface of the insect.

Plastron or Physical Gill

Crisp and Thorpe give us a very clear picture of the physics of the surface respiratory systems of certain under-water insects which rely on the adhesion of air for their function. They describe the general compromise in dimensions of the structure of the plastron between the quantity and diffusibility of air adsorbed and the strength, shape and number of hairs. They show that, with the hairs bent so that the tips are horizontal to the surface of the insect, pressures up to 3½ atm. can be withstood by the plastron, and pressures can still be held even with a contact angle as low as 20°. A plastron consisting of hairs arranged vertically can only resist pressures when the contact angle is greater than 90°. Attention is drawn to the fact that in the formation of the plastron water must be ejected from between the hairs, although when the air is driven out from here by artificial pressure recovery is obtained only by drying. This raises the whole question of the contact angles between air, water and a lipo-protein substrate. If the lipoid is orientated in a condensed monolayer on top of the protein, high contact angles could be obtained. Recently [5] it has been shown that when the CH_3 groups are close packed on the surface of a monolayer, the surface is both hydrophobic and oleophobic, and the receding and advancing angles are the same. Small disorder in the CH_3 group arrangement permits oils but not water to spread. Further disorder in the lipoid molecular arrangement enables finite contact angles to be obtained both with oil and water. Mixed lipoid and protein monolayers could give finite contact angles both with oil and water, and give rise to differences in the advancing and receding contact angles by occlusion of water, as discussed in the section on the fundamental aspects of this problem.

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[2] Bickerman, *Proc. Roy. Soc. A*, 1939, **170**, 130.
[3] Dervichian, *J. Chem. Physics*, 1939, **7**, 931.
[4] Hess, Philipoff and Kiessig, *Kolloid-Z.* 1941, **96**, 225.

Department of Colloid Science,
The University,
Cambridge.

[5] Bigelow, Pickett and Zisman, *J. Colloid Science*, 1946, 1, 513.

THE INSECT CUTICLE AS A LIVING SYSTEM

BY V. B. WIGGLESWORTH

Received 16*th January*, 1948

For all its purposes the living cell makes use of compounds whose physical and chemical properties are more or less well known. The synthesis and deposition of these compounds result from the controlled activity of the cell. To a varying extent such products remain part and parcel of the mother cell, the physiological activity of which may serve to enhance or modify the natural properties of the inert materials. The aim of this paper is to summarise the properties of the materials composing the cuticle; to describe how they are laid down; and in particular, to discuss the extent to which in the living insect the cuticle as a whole may be considered to be alive. To consider, in brief, which of the problems of the insect cuticle already fall within the province of the physical chemist; which are still the preserve of the biologist.

The insect cuticle varies enormously in structure and properties in different insects and even in different parts of the same insect; but here we can attempt only a generalised description (Fig. 1). The cuticle is always the product of a single layer of epidermal cells applied to its inner surface. From the cells there run convoluted filaments (the pore canals) which reach almost to the outer surface. There is always a very thin brown or amber-coloured epicuticle, hard and refractile, in which the pore canals end without opening to the exterior, and a soft, colourless and laminated endocuticle. The outer half or one-third of the latter is often hard, brittle and amber-coloured like the epicuticle and is then termed the exocuticle. The cuticle is pierced at frequent intervals by the ducts of dermal glands. Its total thickness may vary from one or two microns up to 240 μ or more.

The cuticle contains perhaps 30–40 % water, 20–30 % chitin, 20–30 % of protein and 3–5 % of ash, chiefly calcium salts.[1] Chitin is usually present in higher concentration, say 60 % of the dry weight, in the endocuticle, protein in substantially greater quantity in the exocuticle. The long-chain chitin molecules are associated in elongated micellæ which are arranged at random in parallel, horizontal planes. The chitin and protein are intimately associated; indeed it has been suggested by some authors that there may be alternating " monolayers " of chitin and protein, or that the chitin and protein may form interpenetrating lattices.[2] The bulk of the protein, " arthropodin," is somewhat reminiscent of sericin. It is a globular protein containing tyrosine and tryptophane with no glycine, little serine and no carbohydrate. There is a small amount of a second protein of the muco-polysaccharide type.[3]

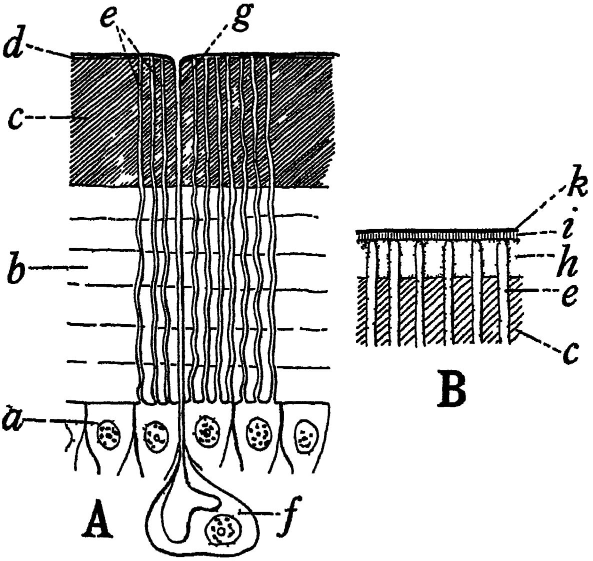

FIG. 1.—A—section through a typical insect cuticle, schematic The pore canals are shown only in the middle region. B—schematic section of the outermost layers. *a*, epidermal cells; *b*, laminated endocuticle of soft protein and chitin; *c*, exocuticle of sclerotin and chitin; *d*, complex epicuticle; *e*, pore canals running from the cells; *f*, dermal gland; *g*, duct of dermal gland; *h*, cuticulin layer; *i*, wax layer; *k*, cement layer.

By virtue of the arrangement of the chitin micellæ, the endocuticle shows form birefringence when viewed tangentially. But in the exocuticle it is isotropic because the amber material which fills the spaces between the micellæ has a refractive index approximating to that of chitin. This amber material is called sclerotin. It consists of protein which is rendered highly insoluble by the incorporation of numerous primary valence cross-linkages between adjacent polypeptide chains. These linkages are effected by means of quinones which block the amino or imino groups and tan the protein, converting a soft, colourless, soluble material into a hard, insoluble, reddish-brown lipophile substance.[4] The vertical pore canals which traverse these layers may contain fluid or cytoplasmic contents, or they may be converted into filaments of chitin.[5] [6] In the hard type of cuticle there is evidence that in the exocuticle they come to contain tanned protein.[7]

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[1] Lafon, *Ann. Sci. Nat. Zool*, 1943, **5**, 113.
[2] Fraenkel and Rudall, *Proc. Roy Soc.* B, 1947, **134**, 111.
[3] Trim, *Biochem. J.*, 1941, **35**.
[4] Pryor, *Proc. Roy. Soc.* B, 1940, **128**, 393.

The epicuticle is a complex structure made up of several layers (Fig. 1, B). The basic layer, visible in microscopic sections, is amber-coloured like the exocuticle and usually not more than 1 μ thick. Like the exocuticle it is highly resistant to solution in cold concentrated mineral acids; but unlike the exocuticle, if broken down by warming in conc. HNO_3 saturated with $KClO_3$, it gives rise to quantities of oily droplets. It is believed to consist of condensed lipoproteins subsequently tanned with quinones. This material is called "cuticulin."[8] Overlying the cuticulin is a thin layer of wax in crystalline form, perhaps a quarter of a micron thick; and this in turn is protected by a very thin layer of "cement" poured out over the surface from the dermal glands. The cement also seems to consist of tanned protein, perhaps associated with lipides.[7]

The cuticle provides the jointed skeleton of insects, to which the muscles are attached. Its various parts need, therefore, to be rigid, flexible or elastic according to their function; but with all this the cuticle must be waterproof. It is with the water relations that we are here concerned.

The sclerotin of the exocuticle belongs, like keratin, to the "dry" type of proteins, in which the chains are bound together by cross-linkages that block the hydrophilic groups. Consequently it is not dependent on the inbibition of water to maintain its form.[4] It is well known that membranes of such materials, if they are allowed to dry, will prevent the transpiration of water. This phenomenon can be seen in the insect. The larva of the wireworm *Agriotes*, when first removed from the soil, loses water very rapidly; but if it is exposed in a dry atmosphere, the rate of water-loss quickly diminishes.[9]

It is, however, the epicuticle which is mainly responsible for the prevention of water-loss. The moisture in the cuticle comes very near the surface. If the insect is immersed in liquid paraffin, minute droplets of water soon appear over the surface of the cuticle, not only in the soft parts, but in many places where an exocuticle is present.[10] And if the insect is immersed in a mixture of kerosene and ethyl alcohol,[11] or other mixtures with suitable partition coefficients in respect to water [12] the droplets will swell and swirl as though the insect were effervescing.

It is indeed well established that it is the superficial layer of the epicuticle which prevents the passage of water. In the cockroach there is a very soft wax or grease freely exposed on the surface. If minute droplets of water are sprayed on to the cuticle this grease spreads over them (as a film sufficiently thick to show interference colours) and will prevent them evaporating for hours. If the temperature is raised above 30° C. this film suffers a change of phase, water molecules will pass through, and the droplets of water and the whole insect dry up.[13]

The same thing happens in other insects, but the waxy materials concerned have mostly a much higher melting point. Fig. 2 shows some examples. The increased loss may happen around 30–37° C., temperatures at which the insect is still alive, or it may not begin until the temperature reaches 50–60° C., when the insect has, of course, been killed by the heat.[9] The waterproof properties of insects can be reproduced by applying the extracted waxes to artificial membranes.[14]

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[5] Dennell, *Proc. Roy. Soc.* B, 1946, **133**, 348.
[6] Dennell, *Proc. Roy. Soc.* B, 1947, **134**, 485.
[7] Wigglesworth, *Quart. J. Micro. Sci.*, 1948 (in press).
[8] Wigglesworth, *Proc. Roy. Soc.* B, 1947, **134**, 163.
[9] Wigglesworth, *J. Expt. Biol.*, 1945, **21**, 97.
[10] Wigglesworth, *Bull. Entomol. Res.*, 1942, **33**, 205.
[11] Hurst, *Nature*, 1940, **145**, 462.
[12] Wigglesworth, *Nature*, 1941, **147**, 116.
[13] Ramsay, *J. Expt. Biol.*, 1935, **12**, 373.

The freely exposed grease on the cockroach is largely removed and the insect rendered more permeable to water, by adsorption in contact with fine dusts. This does not happen with the other insects, because the waxes are too hard at normal temperatures and because they are covered by the cement layer. They are removed, however, if the surface is rubbed lightly with fine abrasive dusts, such as alumina, and then the insect loses water rapidly.

This treatment causes no visible injury to the cuticulin layer of the epicuticle. But the extent of the abraded areas is readily demonstrated by immersing the insect in ammoniacal silver hydroxide. This is reduced by the polyphenols which occur plentifully in the outer layers of the cuticle and which are presumably the precursors of the quinones which tan the cuticular proteins. By means of this reaction it is possible to show that only the most superficial abrasion is needed to destroy the impermeability of the cuticle.[9] Insect larvæ living in the soil are naturally so scratched that they normally lose water very rapidly when removed from their humid environment. The wireworm *Agriotes* (Fig. 1) is an example of this.

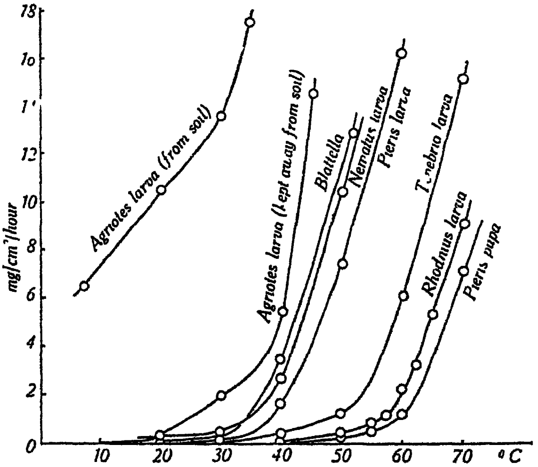

FIG. 2.—Rate of transpiration of water from certain dead insects in relation to temperature.

The insect grows by means of a series of moults. A new and larger cuticle is laid down beneath the old cuticle; the chitin and protein in the inner layers of the old cuticle are then digested and absorbed, and the outer layers are cast off. It will be well to describe briefly the deposition of the cuticle which takes place at the times of moulting.[7] [8]

After dividing and arranging themselves as an even layer, the epidermal cells first lay down the cuticulin layer. There is some evidence that the lipoproteins which compose this layer are synthesised by specialised ectodermal cells called oenocytes. The lipoprotein then undergoes some kind of condensation, perhaps as the result of denaturation of the protein, and its solubility is diminished. It has the appearance of a homogeneous membrane, but it is probably pierced by cytoplasmic filaments from the epidermal cells, the pores being closed superficially by the cell membrane alone. For if treated with ammoniacal silver soon after its deposition, minute silver-staining droplets, regarded as polyphenol droplets, appear on the surface; and running from them through the cuticle to the cells are silver-staining filaments.

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[14] Beament, *J. Expt. Biol.*, 1945, **21**, 115.

These droplets enlarge and fuse until the new cuticle is covered with a more or less continuous "polyphenol layer." Meanwhile the exocuticle is being laid down and the products of digestion of the old skin are absorbed through the new. At this time the cuticle is freely permeable to water; but during the last few hours before the old skin is shed, the wax is secreted by the epidermal cells. It is presumably discharged through the pore canals and eventually forms a practically continuous layer over the surface of the polyphenols, so that when the old skin is thrown off, the insect is almost completely waterproof and its surface is completely hydrophobic.

Within the next half hour or so, the dermal glands pour out the cement layer over the surface, so that it becomes temporarily hydrophilic. Then hardening and darkening occur. These processes result from the action of polyphenol oxidase on the polyphenols, with the production of quinones which tan the proteins. The dark colour is largely due to the chromophore groups in the tanned protein itself; [4] but in some instances there is probably a formation of true melanin from tyrosine at the same time. The enzymic changes during normal moulting have not been studied, but in the special case of the hardening of the puparial shell of fly larvæ, a good deal is known about the distribution and control of the enzymes and substrates concerned.[15] Finally, during the days and weeks which follow moulting, the endocuticle is secreted.

It is quite evident that throughout the period of its deposition the cuticle is very much alive. There has been some controversy in the past as to whether the cuticle is formed by secretion from the cell or by transformation of its outer layers. It is generally agreed now that there is no real distinction between the two processes; but in view of what has been learned recently about the deposition of the epicuticle, it is perhaps reasonable to regard the surface of the cuticulin layer in the moulting insect as the surface of the cell.

The question arises, how far does the cuticle remain alive after moulting? It may be that in some of the blackest and horniest of cuticles the outer layers are totally inert. But in many insects, even when an exocuticle is present, that is not so. Superficial abrasions, causing no visible injury to the cuticulin layer, which remove the cement and the wax and destroy the impermeability to water, cause the epidermal cells below, separated perhaps by some 30 μ of cuticle, to react as though they had been wounded. They show renewed activity and proceed to secrete, presumably by way of the pore canals, a fresh layer of wax which restores the impermeability (a new layer of cement, which arises from the dermal glands, is not produced).[9] Likewise, if certain oils, particularly if they contain some oleic acid, are applied to the surface of the cuticle, they are actively absorbed and appear as droplets in the underlying cells.[10]

And there may be an active uptake of water. We have regarded the waterproofing of the cuticle as a wholly passive affair. But certain insects (though by no means all) are able to absorb water from an atmosphere with a R.H. of 85 % or less. And in even drier atmospheres, although the water content will not increase, the rate of loss is lower in the living animal than in the dead because it is further restricted by the secretory activity of the cells. These remarkable phenomena have been studied in some detail in the ticks by Lees.[16] [17] We must therefore regard the insect cuticle as a living tissue, in which the material basis is not only maintained by the cells but its properties supplemented by their physiological activity.

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[15] Dennell, *Proc. Roy. Soc.* B, 1947, 134, 79.

Summary

The insect cuticle is " alive " almost to the surface. Cytoplasmic filaments from the epidermal cells run in pore canals through the endocuticle and exocuticle and come close to the surface of the epicuticle. The waterproof properties reside in the wax layer of the epicuticle.

Four layers have been recognised in the epicuticle.

(i) The epidermal cells first lay down a thin membrane of lipoprotein which is subsequently tanned by quinones (" *cuticulin layer* ").
(ii) This appears to be penetrated by the pore canals which discharge on to its surface a layer of material rich in silver-reducing substances—probably dihydroxyphenols in insoluble form (" *polyphenol layer* ").
(iii) Wax is then secreted through the pore canals to form a waterproof film over the surface of the polyphenol layer (" *wax layer* ").
(iv) Finally, a protective secretion is poured out over the surface of the wax by small dermal glands whose ducts pierce the cuticle at intervals (" *cement layer* "). The cement probably consists of protein tanned by quinones and intimately associated with lipides of some kind.

According to the theory of Pryor, oxidation of the polyphenols results in the hardening of the exocuticle (and of the cuticulin layer of the epicuticle) through the tanning of their proteins by quinones.

There are wide variations in properties of the cuticle in different insects or different parts of the same insect. The temperature at which the wax layer becomes permeable to water may range from 30° c. to nearly 60° c. in different species. In the cockroach and its allies it is a soft mobile substance apparently without a protective layer of cement. The degree of hardening (tanning) of epicuticle and exocuticle varies. In many insect larvæ living in the soil the surface of the cuticle is so abraded that they are always more or less permeable to water.

Superficial injuries to the cuticle (abrasion by fine dusts) render it permeable to water. Impermeability may be restored by the secretion of more wax by the epidermal cells. In some cases the cells themselves play an *active* part in controlling the entry and escape of water. The integument is a living tissue.

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[16] Lees, *Parasitology*, 1946, **37**, 1.
[17] Lees, *J. Expt. Biol.*, 1947, **23**, 379.

THE ROLE OF WAX LAYERS IN THE WATERPROOFING OF INSECT CUTICLE AND EGG-SHELL *

BY J. W. L. BEAMENT

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The water-impermeable barrier of the insect cuticle is to be found in the outermost layers of the cuticle. This fact has been known for many years [1] [2] but considerable complications arose through two contrasting observations. Bergmann [3] and others demonstrated that lipoid material could be removed from the cuticle by the action of wax solvents ; further, Chibnall *et alii* [4] had made detailed chemical analyses of such lipoids and shown them to consist of long-chain fatty acids, alcohols and esters with chain length of the order C_{30}. On the other hand, lipoid could also be obtained from the outer cuticle layer by the action of fused alkali or oxidising acids; this indicated a cuticle structure containing fatty material combined *chemically* with other components.

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[1] Kuhnelt, *Zool. Jahrbuch*, 1928, **50**, 219.
[2] Wigglesworth, *Quart. J. Micro. Sci.*, 1933, **76**, 269.
[3] Bergmann, *Ann. Entom. Soc. Amer.*, 1938, **31**, 315.
[4] Chibnall *et alii*, *Biochem. J.*, 1934, **28**, 313.

* Unless other reference is made in the text, this contribution is based on : Beament, *J. Expt. Biol.*, 1945, **21**, 115.

The explanation of these opposed hypotheses was provided by Wigglesworth,[5] who proposed that the cuticle was covered by a thin layer of waxy material, which waterproofed it and [6] confirmed that in the bug *Rhodnius* there is also a lamina of material beneath this wax, which contains lipoid combined chemically to protein (the " cuticulin " layer).

The biological evidence for the presence of wax layers has been outlined by Wigglesworth [5] [6] and referred to in that author's contribution to this Discussion. In particular, wax solvents, abrasives and wax detergents will render insects liable to desiccation and their cuticle permeable to dyes. Wigglesworth [5] also extended the work of Ramsay [7] who had measured the rate of evaporation for the cuticle of the cockroach, *Periplaneta americana*, at various temperatures. Ramsay showed that at a particular and specific temperature, transpiration increased suddenly. He proposed that this was due to some physical change in the properties of a greasy substance to be found on the cuticle surface. Wigglesworth [5] carried out similar experiments with many larval and adult insects, representing the main orders; he demonstrated that each species showed an abrupt increase in the water-permeability of the cuticle at temperatures, varying between 25 and 60° c., which were constant for any one species and stage of development. He proposed that this " critical temperature " corresponded to a change in the wax layer on the cuticle.

The cast skins of the majority of insects consist of the whole of the epicuticle, together with some fragments of exocuticular material. As compared with whole cuticle preparations, cast skins are almost free of perforations, since glandular and similar invaginations are intact. If such skins are mounted as membranes, separating water from a dry atmosphere, they show the same order of impermeability as the cuticle of intact insects at corresponding temperatures. If on the other hand, a cast skin is treated with a boiling wax-solvent, so that physically bound lipoid is removed, then the permeability at lower temperatures is vastly increased. Now this lipoid-free cast skin still contains lipoids [6] which can be released by chemical decomposition. Clearly, therefore, it is the lipoid which can be extracted, and *not* the chemically bound material, which is waterproofing the cuticle.

If numbers of clean cast skins from one species of insect are exhaustively extracted with boiling chloroform, the waxy materials may be obtained from the solvent. If the wax is distributed as an even layer over the cuticle surface, determination of the cuticle area provides an estimate of the thickness of such a layer. Although the surface area of an insect cannot be measured with great precision, the amount of wax per unit area of cuticle is remarkably constant for any one species of insect, and the actual thickness lies between the limits 0·2–0·3μ for a great many insects. This value would correspond to some thirty monolayers of orientated wax molecules. The thickness of the wax layer bears no relation to the thickness of the particular cuticle or epicuticle from which it is extracted.

The majority of the extracted lipoids are white or yellow waxes, similar in consistency and probably in composition to beeswax,[8] chermes wax,[9] etc. A few genera, notably cockroaches, locusts and Ixodid ticks, yield a more mobile grease. The waxes vary in melting point from 30–70° c., and these temperatures are consistently a few degrees *above* the critical temperature at which the respective source insects become freely permeable to water. Thus the phenomenon cannot be explained by postulating that a wax layer *melts* at the critical temperature.

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[5] Wigglesworth, *J. Expt. Biol.*, 1945, **21**, 97.

[6] Wigglesworth, *Proc. Roy. Soc.* B, 1947, **134**, 163.

[7] Ramsay, *J. Expt. Biol.*, 1935, **12**, 373.

[8] Lewkowitsch and Warburton, *Chemical Technology of Oils, Fats and Waxes.* 1921, **1**, 317 *et seq.*

[9] Alexander, Kitchener and Briscoe, *Trans. Faraday Soc.*, 1944, **40** 10.

The extracted waxes can be deposited from a dilute solution in chloroform to form a layer on various membranes. The degree of waterproofing which such a layer of wax confers on a membrane is related to the chemical nature of the membrane surface. Proteinaceous membranes initiate more impermeable layers than do inorganic materials, while tanned proteins (such as gelatine treated with *p*-benzoquinone) are quite efficient. But waterproofing of the same order as that of the insect of origin, may be obtained by depositing comparable thicknesses of wax on membranes of insect cuticle. Such membranes can be prepared by extracting butterfly wings, cicada wings, pupal wing cases, etc., in boiling chloroform and depositing the wax on the external surface. This waxed side is exposed to a dry atmosphere in a membrane holder filled with water.

When the variation of water permeability with temperature is investigated, these waxed insect membranes show sudden increases at temperatures corresponding to the critical temperatures of the insect from which the wax was obtained, and not to the values for the insects providing the substrate membrane. Similar, if less sharp, changes may be recorded on artificial membranes (due partly, perhaps, to the lesser degree of initial impermeability).

If "inert insecticidal" dusts, such as fine-grade alumina are sprinkled over the surface of a waxed cuticular membrane, no increase in water-transport is produced. In contrast, should a fine layer of dust be moved over the surface of the wax by strokes of a camel-hair brush, there is an immediate and considerable increase in permeability. The dusts are evidently acting by abrading the wax and not by adsorbing their substrate.

When detergents are spread over the surface of a waxed membrane, the permeability of the system is increased; a series of detergents have the same order of effectiveness on waxed membranes as they have on living insects, although it must be remembered that the wax of the insect may be protected by a cement layer.[6]

A composite layer of chloroform-extracted insect cuticle and of wax, and an intact insect cuticle behave very similarly; in particular, it is the behaviour of the species from which the wax was obtained which is reproduced. This similarity provides considerable evidence for supposing that the structure of the waterproofing mechanism is very similar in the two compared systems. Further investigation has revealed the precise nature of waterproofing and the physical processes causing the "critical temperature" phenomenon.

It has been demonstrated [9, 10] that the water impermeability conferred on a membrane by beeswax and by insect waxes is not linearly proportional to the thickness of the wax covering the membrane; a considerable measure of impermeability is obtained with the initial layer of wax and additions of lipoid beyond a thickness of the order 20–200$m\mu$ do not produce an appreciable decrease in permeability. It may perhaps be held that experimental conditions would be inefficient: that the wax layer would be free from pinholes only when such a critical thickness is exceeded. But the phenomenon is still very definite even after the membrane has been heated above the melting-point of the wax, so that the lipoid could spread over any gaps (permeability measurements being repeated at room temperature). The actual permeability is not of the same order as a membrane which has been abraded. It is also interesting to note at this point that films of *n*-paraffin wax give linear curves for permeability against thickness of layer measurements.

These experiments would at least indicate that some property of the interfacial wax layer is especially responsible for waterproofing. This theory is reinforced by some experiments carried out with the waterproofing grease from the cuticle of the cockroach. Wigglesworth [8] found that stationary "inert" dusts have no effect on the rate of water-loss from intact insects which have hard cuticular

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[10] Beament, *J. Expt. Biol.*, 1945, **21**, 115.

waxes. But dusts adsorb much of the mobile grease from the cuticle of the cockroach and permeability is somewhat increased. This increase in transpiration is *not* comparable to the great change produced by washing a cockroach with chloroform.

If a drop of grease from the cuticle of a cockroach is placed in the centre of a circular membrane of extracted insect cuticle the permeability of the system falls. A permeability–time curve (Fig. 1) shows two distinct phases; during the six hours following the addition of the drop, permeability falls rapidly to a comparatively low value. But it is not until 120 hours later that the membrane attains a steady state, throughout which time the permeability continues to fall at a slow rate. The final figure obtained corresponds closely to the permeability of the intact cockroach cuticle (both systems having approximately 0·6μ of grease over the surface).

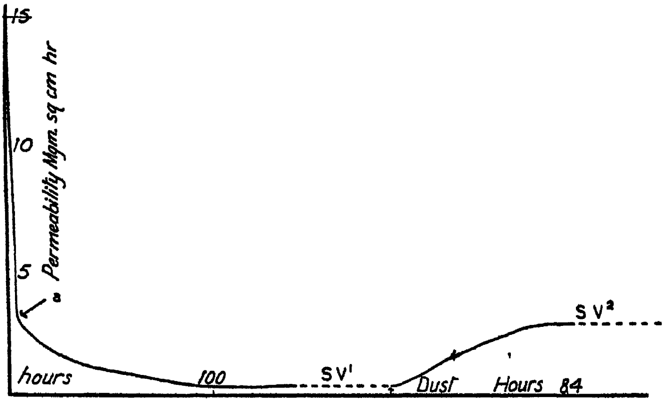

FIG. 1.—Graph showing permeability changes when a droplet of waterproofing grease from the cockroach is applied to the centre of a membrane of wax-free cuticle. Original permeability 15 mg /sq. cm./hr, dropping over first six hours to value approximately 3 mg./sq. cm /hr. (*a*), and slowly to steady low value (S.V.¹). After application of adsorptive dust (*Dust*), permeability increases to steady value (S.V.²) equivalent to that at (*a*).

If the membrane is now sprinkled with "inert" dust, which *is* capable of adsorbing this mobile grease, permeability rises to the "6-hourly" value; no amount of extra clean dust or abrasion will increase this figure. Washing with chloroform, however, restores the permeability of the system to a value approaching the initial transpiration of the ungreased membrane.

These results may be explained as follows. At six hours, the membrane surface has been covered by one complete, orientated and tightly packed monolayer of grease; additional waterproofing is obtained by the even distribution of the bulk of the grease over the monolayer. Although inert dust can adsorb the grease, it cannot compete successfully for this monolayer. The physico-chemical forces which attract the polar groups of the lipoid molecules to the tanned protein substrate of the membrane are stronger than those forces which would attract the grease onto the dust particles. Hence the transpiration value at six hours after spreading, or after dusting, represents approximately the waterproofing conferred by a monolayer of cockroach grease. Chloroform, however, has great affinity for the liquid molecules, and is capable of detaching the monolayer.

It is well known that a monolayer of long-chain molecules, spread over the surface of water, is capable of depressing evaporation very considerably. It is perhaps interesting to note that Ramsay [7] showed that a droplet of water placed on the cockroach cuticle does not evaporate at all quickly; it is protected by a thin film of grease which spreads over it. Danielli [11] and others have suggested that cell surfaces, including erythrocyte membranes, are composed of layers of

[11] Danielli, *Cold Spring Harbour Symp.*, 1938, 7, 393.

lipoid materials orientated into monolayers at protein surfaces. Now the main constituents of the insect waxes so far investigated appear to be polar molecules, such as acids, alcohols and esters, with only a small percentage of non-polar paraffins. Presumably polar molecules are important in the organisation of a monolayer at the epicuticle surface and any paraffins will take up similar alignment through the action of van der Waals' forces along the carbon chain of the polar molecules.

Preliminary X-ray analysis [12] indicated that in a film of beeswax without substrate, molecules were aligned into crystallites of random distribution; if wax was deposited onto a silk meshwork, the molecules were highly organised and oriented perpendicular to the direction of the silk fibres along the wax-silk interface.

These results lead us to the conclusion that it is the innermost monolayer of the wax lamina on insect cuticle—a layer which is highly organised by the cuticle surface and closely packed—which is responsible for the greater part of waterproofing. No doubt, as X-ray and birefringence studies indicate, this monolayer will itself organise a degree of orientation in the layer of lipoid above it. Orientation would become less and less as the distance from the original substrate increased (especially as the wax is not a homogeneous material and contains molecules of varying length). Such a phenomenon would explain the non-linear nature of the permeability—wax-thickness curves described above. It is perhaps not without significance that the majority of insects secrete a minimal thickness of wax (0·25μ) compatible with maximal waterproofing.

An explanation of the sudden changes in permeability at the critical temperature is now possible. Changes in optical properties (indicating crystal changes) occur a few degrees below the melting points of fragments of extracted waxes. Pieces of wax placed in the air-water interface of a waterbath spread slowly at temperatures below their melting-points, as shown by the movement of lycopodium powder on the water surface. If *Rhodnius* cuticular wax, or beeswax, is deposited as a film on a glass coverslip, contact angle measurements with water droplets on the waxy surface indicate that it is quite hydrofuge.[10] No change is occasioned by immersing the film in water at temperatures below the critical temperature; the contact angle is measured each time against the dry wax to obviate the effect of adsorbed water. But if the film is immersed at temperatures between the critical temperature of the wax and its melting-point, the dry wax becomes permanently more hydrophilic. Obviously, at the higher temperature, the wax surface has been organised so that the polar groups are exposed, which produces the hydrophilic surface. Contact angles of water droplets on similar wax films on glass, have been measured over a range of temperatures; they indicate a reorientation of wax molecules, so that polar groups are exposed, at temperatures which for each species is very close to the critical temperature.

All this evidence indicates that the critical temperature occurs when a monolayer of mixed waxes starts to disorientate or reorientate. Müller [13] described changes in the crystal spacings of *n*-paraffin waxes when heated to "transition points" well below the melting-point of the wax. It is, therefore, suggested that the phenomenon of increased permeability of insect cuticle at critical temperatures is due to the disorganisation of the tightly packed monolayers on the tanned protein substrate of the epicuticle. When the molecules of lipoid reach such a degree of kinetic oscillation that this may amount to complete rotation, the van der Waals' forces are disrupted and in the subsequent arrangement water may pass through the intermolecular spaces more readily. Ramsay [7] demonstrated such a phenomenon, using the cockroach. It has been indicated above that a droplet of water placed on the cockroach cuticle becomes enclosed by a thin film of grease. Evaporation from the droplet is very slow, but should the temperature exceed the transition point (critical temperature) the droplet evaporates very quickly.

These principles have also been applied to the waterproofing of insect egg-shells.[14, 15, 16] The eggs of some insects have a wax layer, supported by a tanned protein substrate, on the *inside* surface of the shell layers; this wax layer protects the eggs from desiccation. Their properties are identical to those of the cuticular wax layers and show sharp transition points. Other eggs, such as those of the Argasid and Ixodid ticks [17] have wax distributed over the external surface of the egg-shell and the situation is very similar to that of cuticular lipoids. Again these shells often contain laminæ of various kinds of lipoproteins, with a high content of chemically combined lipoid. The egg-shell of *Rhodnius* [18] has three such layers, none of which is a barrier to water if the all-important wax layer has been destroyed.

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[12] Greenough and Beament (unpublished work).

[13] Müller, *Proc. Roy. Soc.* A, 1932, 138, 514.

Beament [19] has recently investigated the changes in the permeability of the *Rhodnius* egg-shell during the development of the embryo. A layer of protein is secreted, which covers the inside of the shell and waterproofing wax layer. This protein is later *impregnated* with a waxy material which can be removed by chloroform. The resultant system is certainly capable of considerable resistance to the passage of water, but it does not give a sharp transition point on recording permeability changes at various temperatures. The properties, when investigated by poisons, abrasives, detergents and the penetration of dyes, are altogether different from those of the normal type of waterproofing layer, which is a discrete lamina of wax. It is very interesting to note that both types of waterproofing mechanism may exist in the same set of membranes and that physical, chemical and biological methods as outlined above will distinguish clearly between waterproofing by a wax *layer* system and by a protein *impregnated* with wax.

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[14] Beament, *Nature*, 1946, **657**, 370.
[15] Beament, *Proc. Roy. Soc* B, 1946, **133**, 107.
[16] Beament (unpublished work)
[17] Lees and Beament, *Quart J. Micro Sci.*, 1948 (in press)
[18] Beament, *Quart. J Micro Sci*, 1946, **87**, 393.
[19] Beament, *Bull Entom. Res.*, 1948 (in press).

ISOLATION OF A WAX-LIKE MATERIAL FROM THE SHELL OF THE GRASSHOPPER EGG

By Eleanor H. Slifer

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The importance of a layer of wax on the surface of the cuticle in the control of water-balance in insects has been emphasised during the past few years.[1, 2, 3, 4, 5] In 1946, Slifer [6] reported that the embryonic diapause of the grasshopper, *Melanoplus differentialis*, could be broken by treating the eggs with xylol, etc. The results of a series of experiments led to the conclusion that the action of these solvents was at the hydropyle and that they dissolved away from this area a waxy material which, during diapause,

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[1] Beament, *J. Expt. Biol.*, 1945, **21**, 115.
[2] Ludwig, *Physiol. Zoöl.*, 1946, **19**, 355.
[3] Wigglesworth, *J. Expt. Biol.*, 1945, **21**, 97.
[4] Wigglesworth, *Experientia*, 1946, **2**, 1.
[5] Wigglesworth, *Proc. Roy. Soc.* B, 1947, **134**, 163.
[6] Slifer, *J. Expt. Zool.*, 1946, **102**, 333.

prevented the entrance of the water needed by the embryo to complete its development. While this paper was in press, a note by Beament [7] appeared in which he stated that the inner surface of the egg shell of *Rhodnius prolixus* is waterproofed by a thin layer of wax. Several months later, [8] [9] [10] Beament described in detail the complex structure of the chorion of this egg and the manner in which it is waterproofed. The wax layer present on the inner surface of the chorion when the egg is laid he calls the primary wax layer. He also asserts that there is some evidence that a secondary wax layer is secreted later on the embryonic membranes which are formed just below the chorion.

Beament [8] isolated a waxy material from the shells of *Rhodnius* eggs which had hatched. He extracted vacated shells with boiling chloroform and obtained a white wax upon evaporation of the solvent. The amount present in a single egg, if evenly spread, is sufficient, he calculates, to form a layer approximately 0·46 μ in thickness. This, he thinks, may represent the combined thickness of the two layers, primary and secondary, mentioned above.

Since Beament had succeeded in isolating a wax from *Rhodnius* eggs it seemed possible that this might also be done with those of *Melanoplus*, particularly since experimental work had already suggested that waxes were present. This paper deals with the isolation of such a wax, certain of its properties, its distribution on the surface of the egg and the amounts obtained from eggs in diapause, from eggs in which diapause had been broken by cold and from eggs at hatching.

Method of Extracting the Wax

When the first experiments were undertaken to determine the effects of xylol on diapause in the grasshopper egg, the xylol which had been used to treat the eggs was allowed to evaporate. A film of white, waxy material remained in the dish. This suggested, naturally, that the xylol had removed from the surface of the egg some material which was effective in producing diapause.

Carbon tetrachloride, like xylol, will break diapause [6] and, since it has a considerably lower boiling point, was chosen in preference to xylol for the extraction of the wax All of the carbon tetrachloride (Merck C.P) used was redistilled in a Pyrex glass still. When a 20-cc. sample of this was allowed to evaporate no visible or weighable residue remained.

Since the wax is present in very small amounts it was necessary to use large numbers of eggs in each experiment. The pods were gently broken up in water and all sand, debris and spoiled eggs removed. After many washings in distilled water each egg was examined under a dissecting microscope to be certain that an embryo was present and that the chorion was free from blemishes.

In experiments with diapause eggs and with eggs in which diapause had been eliminated by exposure to cold, the chorion was removed by hand after alternately wetting and drying the eggs several times.[11] The chorions were dried overnight, or longer, above $CaCl_2$ and then extracted with CCl_4 according to the procedure to be described below. The eggs from which these chorions had been removed, and which had been kept meanwhile in distilled water, were dried on filter-paper and themselves extracted with CCl_4 This removed any wax which might be present on the chitinous cuticle, of which the hydropyle is a specialised part.

Vacated shells were secured by allowing cold-treated eggs to hatch. The shells left behind by the young grasshoppers were picked out, counted, dried over $CaCl_2$ and extracted with CCl_4. Each vacated shell includes not only the chorion but, adherent to its inner surface, the thin yellow layer of the chitinous cuticle.[12] Any wax which is present on the inner surface of the chorion or the outer surface of the chitinous cuticle should be present in the extract.

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[7] Beament, *Nature*, 1946, **157**, 370.

[8] Beament, *Proc. Roy. Soc.* B, 1946, **133**, 407.

[9] Beament, *Quart. J. Micro. Sci.*, 1946, **87**, 393.

[10] Beament, *J. Expt. Biol.*, 1947, **23**, 213.

[11] Slifer, *Biol. Zentr.*, 1932, **52**, 223.

In certain experiments, whole eggs were extracted with CCl_4 and in others, part or all of the chorion was removed with NaOCl [13] before extraction.

Chorions and vacated shells were extracted with 6 cc. of redistilled CCl_4 for 15 min. and the fluid filtered onto a weighed watch glass. This was repeated three times and all of the CCl_4 collected on the same watch-glass, where it was allowed to evaporate. Immediately afterwards, or on the following day, this entire procedure was repeated. Finally the chorions or shells were treated twice, for 5 min. each, with 12 cc. of boiling CCl_4 and the hot extract caught on a third watch-glass. The watch-glasses, after the evaporation of the solvent, were weighed. The eggs from which the chorion had been removed were, meanwhile, extracted four times, for 15 min. each, with 6 cc. of CCl_4. Hot solvents cannot be used on them for they shrivel if so treated.

Since only a few mg. of wax are obtained from a large number of eggs the error in these determinations is considerable. To check the extent of this, the eggs from 40 pods, after thorough mixing, were divided into two lots and duplicate extractions made. The amount of wax obtained from one sample was 0·0019 mg. per egg and from the other 0·0028 mg. The quantitative results presented in this paper must, therefore, be considered as first approximations only. Perhaps in the future some more satisfactory way of estimating the amount of wax present can be devised.

Properties of Wax Obtained from Surfaces of the Egg

The wax or wax-like material obtained from the chorion and the chitinous cuticle is hard, white and amorphous. It resembles a high melting-point paraffin in appearance and chips readily when touched with a needle. The chips usually show an electrostatic charge and cling to the needle. Melting-point determinations were made with a Fisher-Johns apparatus on samples of wax which were placed on cover glasses, melted and then allowed to stand for at least 24 hr. after they had hardened. During the determination, the wax sample was watched under a microscope. As is often the case with natural waxes, which are usually mixtures, melting occurred over a range rather than at a point. As 46° c. was reached a few droplets appeared on the surface of the sample and at 56° c. the entire mass softened. At 60° c. melting was fairly rapid and between 64° and 65° c. nearly all became fluid. In some samples fusion was not complete until 70° c. had been reached. The wax was soluble, at room temperature, in xylol, toluol and chloroform, partially soluble in benzene and little, if at all, soluble in alcohol, ether and acetone.

Amount of wax present at different stages of development.—The results of experiments with eggs in diapause, with eggs in which diapause had been broken by exposure to cold and with shells from eggs which had hatched are given in Table I. The figures in the last column indicate the total amount of wax extracted. It is obvious that if there is any increase or decrease in the quantity of wax present during this period, the method is not sufficiently delicate to detect it.

Localisation of the Primary Wax Layer

According to Beament[8] the primary wax layer is deposited on the inner surface of the chorion by the protoplasm of the *Rhodnius* egg shortly before it is laid. This layer extends across the inner ends of the micropyles, which penetrate the shell, and so waterproofs the egg efficiently even though it is excessively thin. Experiments with *Melanoplus* eggs indicate that these, too, are waterproofed near the time they are laid.

Day-old eggs were removed from the pod, freed of debris and divided into two lots. One lot was placed on dry filter-paper and left there, exposed to the air, for 24 hr. at room temperature. The second lot, after being dried for a short time on filter-paper, was treated with xylol for 15 min., drained and the eggs placed on another piece of filter-paper beside the first set. Within 40 min. the xylol had evaporated from the second lot and every egg was badly shrunken. The untreated eggs, on the contrary, showed relatively little shrinkage even after 24 hr. The most probable explanation for the marked difference in the resistance to desiccation of the two groups of eggs seems to be that in the second lot the xylol had entered through the micropyles or other openings and dissolved the protective layer of wax. Additional evidence was obtained by placing day-old eggs in xylol and watching them under the microscope. In eggs so treated, the micropylar area and that immediately posterior to it becomes translucent instantly. The outermost layer of the chorion anterior to the micropyles is not penetrated by the xylol. Gradually the translucent region increases in size as the xylol passes anteriorly below the outer layers of the chorion. Soon the xylol reaches the anterior pole of the egg and the yolk particles, etc., inside the egg show very clearly through the chorion which has become as clear as glass.

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[12] Slifer, *Quart. J. Micro. Sci.*, 1937, **79**, 493.

[13] Slifer, *Science*, 1945, **102**, 282.

TABLE I

AMOUNT OF WAX EXTRACTED FROM (1) DIAPAUSE EGGS, (2) COLD-TREATED EGGS IN WHICH DIAPAUSE HAD BEEN BROKEN AND (3) VACATED SHELLS OF EGGS WHICH HAD HATCHED.

	Number of chorions, etc , used	Mg. wax per chorion, etc.	Total mg. wax per egg
DIAPAUSE :			
Expt. 1 chorions	788	0·0023	
eggs	577	0·0005	0·0028
Expt. 2 chorions	644	0·0017	
eggs	458	0·0002	0·0019
COLD-TREATED :			
Expt. 1 chorions	1273	0·0025	
eggs	510	0·0004	0·0029
Expt. 2 chorions	1526	0·0022	
eggs	632	0·0000*	0·0022
HATCHING :			
Expt. 1 vacated shells	1800		0·0019
Expt. 2 vacated shells	2335		0·0024

* Trace of residue in watch-glass not weighable.

The chitinous cuticle in *Melanoplus* eggs is secreted by the embryonic serosa between the fifth and, approximately, the sixteenth day of incubation at 25° c. When this has formed, the primary wax layer must then be enclosed between its outer surface and the inner surface of the chorion. Beament,[8] as additional proof for the presence of a waxy layer in this region, states that in the *Rhodnius* egg at hatching the chorion and membranes below it separate readily when the vacated shell is placed in chloroform. The same phenomenon occurs in the grasshopper egg and, in fact, was noted briefly by the present writer in describing the method used to break diapause in this species : " The small bit of chorion left at the posterior tip of the egg usually fell off a few minutes after the egg was placed in the xylol."[6] The chorion drops from the egg as if the cement which attached it to the cuticle had been dissolved away. When an attempt is made to remove this bit of chorion from an egg which has not been treated with xylol it is found that considerable force is necessary to pry it loose.

In another experiment 46-day old diapause eggs, from 40 pods, were cleaned mixed and divided into four groups. In the first group the eggs were left intact, in the second group they were treated briefly with NaOCl so that the outermost layers only of the chorion were removed, in the third group the NaOCl was allowed to act until all of the chorion in the middle region of the egg had dissolved but that at the anterior and posterior poles remained, and in the fourth group treatment with NaOCl was continued until every trace of the chorion was gone. Each group was then extracted with CCl_4 as described above. The results appear in Table II. It will be observed that some wax can be obtained from whole eggs but that not all of it is removed by the treatment. Presumably, this escapes through the micropyles or other small openings in the chorion at the posterior end. When, on the other hand, every trace of the chorion is removed all of the wax is lost with it. These results suggest, again, that the bulk of the wax is present on the inner surface of the chorion.

TABLE II

AMOUNT OF WAX EXTRACTED FROM DIAPAUSE EGGS WITH THE CHORION INTACT, PARTIALLY REMOVED OR COMPLETELY ABSENT.

Condition of egg	Number of eggs used	Mg. wax per egg
Chorion intact	866	0·0012
Outer layers of chorion off	659	0·0018
Chorion off except at tips	634	0·0017
Chorion entirely gone	665	0·0000

An attempt was next made to discover whether the wax was equally distributed on the anterior and posterior portions of the egg. Diapause eggs were treated with NaOCl until the chorion over the middle half of the egg was destroyed while that at the ends remained. The eggs were then divided into three lots. The anterior third of each egg of one lot was dipped into a warm 1 % agar solution and the posterior third of each egg in the second lot was similarly covered. The presence of the moist agar would, of course, prevent the solution of any wax directly beneath it. The third lot was left with no agar. After the agar had solidified and the eggs had been dried, each lot was extracted with CCl_4. The results are given in Table III. We may conclude, so far as our present evidence goes, that the wax is spread rather uniformly beneath the entire chorion.

TABLE III

AMOUNT OF WAX EXTRACTED FROM DIAPAUSE EGGS PARTLY COVERED WITH AGAR OR WITH NO AGAR.

Condition of egg	Number of eggs used	Mg. wax per egg
Anterior one-third covered	366	0·0014
Posterior one-third covered	374	0·0013
No agar	375	0·0019

Thickness of the wax layer.—If the wax is spread evenly throughout the space between the chorion and the chitinous cuticle it becomes possible to calculate the thickness of this layer. In order to do so, it is necessary to determine the area of the inner surface of the chorion. For this purpose the chorion from a diapause egg was cut into several pieces, flattened on a slide, and its image projected onto millimetre paper. The total area was close to 20 mm². If we assume that the specific gravity of the wax is not far from 1, and use the smaller figure for the wax obtained from diapause eggs (0·0019 mg. per egg) in Table I, the thickness of the layer would be about 0·10 μ ; while if we use the larger figure (0·0028 mg. per egg), the layer would be approximately 0·14 μ deep. Unless special techniques were devised to show it, such a layer would not be visible with the highest power of the ordinary microscope. Beament's results[8] for the egg of *Rhodnius* are larger, 0·46 μ, but within the same general range.

Discussion

No evidence has been presented in this paper for the presence of a secondary wax layer such as Beament believes may be formed in the *Rhodnius* egg.[8] Indirect evidence that such a layer occurs in *Melanoplus* already exists. As has been shown earlier,[14] water absorption by the egg begins about the 5th day at 25° c. and continues for 10 days or more. Consequently the hydropyle, which is formed during the 5th, 6th and 7th days, must be permeable to water during this period and then, just before diapause, become impermeable. It seems probable that the hydropyle cells, towards the close of the third week at 25° c., secrete out onto the surface of the hydropyle what may be considered the secondary wax layer.* This would be comparable to the secretion of a wax layer onto the surface of the insect epicuticle, through pore canals, after the deeper layers have been formed.[4, 5]

The question raised earlier [6] as to the manner in which the water-impermeable hydropyle of the egg in diapause is converted into a permeable one at the end of diapause still remains. One suggestion made previously was that a portion of the wax might be destroyed, perhaps by micro-organisms in the soil. If such be the case the amount lost is undoubtedly too small to be detected with such methods as those used here. Another possibility, also mentioned earlier, would be some physical alteration of the excessively thin wax layer. Minute cracks, for example, might develop while the eggs are exposed to low temperatures. Further experimentation is needed here.

Summary

A hard, white, wax-like material has been isolated from the shell of the egg of the grasshopper (*Melanoplus differentialis*). It has a high melting point and is soluble in reagents commonly used to dissolve waxes. At least a portion of this material seems to be deposited on the inner surface of the chorion before the egg is laid. This corresponds to the primary wax layer described by Beament for the egg of *Rhodnius*. A secondary wax layer is probably deposited at the hydropyle when diapause begins. The wax layer, on the assumption that it is uniformly spread over the entire inner surface of the chorion, is approximately 0·10 to 0·14 μ deep. The amount of wax obtained from shells of eggs in diapause, eggs with diapause broken and eggs at hatching ranged from 0·0019 to 0·0029 mg. per egg in different experiments. Since the amount of wax is so small and the error in determinations high, nothing final can be said concerning any changes, during development, in the quantity present.

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[14] Slifer, *Quart. J. Micro. Sci.*, 1938, **80**, 437.

* Cytological studies, not yet complete, suggest that such a secretion does occur at this time.

PASSIVE AND ACTIVE WATER EXCHANGE THROUGH THE CUTICLE OF TICKS

By A. D. Lees

Received 21st January, 1948

The microscopic structure of the tick cuticle is in many respects very similar to that of the insect integument.[1] The cuticle is built up of layers of differing chemical composition. Over the soft parts of the body the epidermis underlies the endocuticle, a pliable fibrous layer of chitoprotein, which is bounded on the outside by the "epicuticle." The latter is itself composite, as in insects, and consists of successive, very thin layers of "cuticulin," polyphenols and wax. In one family of ticks, the Ixodidæ, the wax layer is freely exposed; in the other, the Argasidæ, it is protected externally by a further covering of cement.[2] In all ticks there are pore canals, containing filaments of cytoplasm, which extend through the endocuticle from the epidermal cells; but whether these also penetrate the cuticulin layer of the epicuticle is not yet known with certainty.

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[1] See Wigglesworth, this Discussion.

In dry air at room temperatures, the water lost through the cuticle by transpiration amounts to less than 0·2 % of that lost from a free water surface. This impermeability is in great measure a *passive* property of the cuticle and of the wax in particular. This can be demonstrated in the living tick if the continuity of the wax layer is destroyed by rubbing the cuticle with an abrasive dust. Resistant species, like *Dermacentor andersoni*, which would normally withstand these conditions for many weeks, then dry out completely within a few hours. The escape of water is also greatly hastened if the waxes are extracted from the cuticle with lipoid solvents or detergents.

The properties of the waterproofing agents vary considerably from species to species. And this is reflected in the degree of impermeability of the cuticle. The following is an estimate of the rates of transpiration, expressed in mg./sq. cm./24 hr., in a representative series of engorged ticks which were exposed to dry air at 25° C.: *Ixodes ricinus*, 11·1; *I. hexagonus*, 6·4; *Amblyomma cajennense*, 2·0; *Dermacentor andersoni*, 1·7; *Ornithodorus moubata*, 0·9; *O. delanœi acinus*, 0·2. The cuticular waxes, like those in many insects,[3] [4] undergo transitional changes above the "critical temperature" and permit water to pass more freely. And a further point of resemblance with insects is that the critical temperature (which may or may not fall below the thermal death point) is closely related to the transpiration rate at temperatures within the biological range. In the six species listed above, for example, the approximate critical temperatures are, respectively, 32, 39, 43, 44, 62, and 67° C.[2]

But the passage of water through the cuticle is not regulated only by the physical properties of the integument; it is also profoundly influenced by *active* transfer. This activity is manifested most strikingly in the ability of the living tick to take up water vapour from unsaturated atmospheres and to secrete water into the hæmolymph.[5] Some examples with *I. ricinus* are shown in Fig. 1. If ticks are slightly desiccated at a low humidity (e.g., 50 % R.H.) and are then exposed to saturated air, they gain rapidly in weight and swell visibly as water is transferred to the blood. At 95 % R.H. the desiccated ticks gain water at the rate of 5–10 % of their original weight per day. At 90 % R.H., however, their weight may remain constant or fluctuate slightly from day to day. And at all lower humidities they lose water by evaporation. One consequence of this physiological activity is a departure from Dalton's law at high humidities—for water-loss bears little relation to saturation deficiency.

It is clearly justifiable to refer to this process as "secretion," since the uptake of water proceeds against a gradient of vapour pressure. The osmotic pressure of the blood in *I. ricinus* (the unfed female) is equal to that of a 1·1 % solution of NaCl; and the blood would therefore be in equilibrium with a R.H. of 99·3 %. Yet water can be abstracted from all humidities down to approximately 90 % R.H. This latter point, at which the loss and gain of water is evenly balanced, has been termed the " equilibrium humidity." However, as Krogh [6] has pointed out in the analogous case of the ion uptake by aquatic animals, this condition will resemble a steady state, dependent for its maintenance on the continuous supply of energy, rather than a true equilibrium in the physical sense.

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[2] Lees, *J. Expt. Biol.*, 1947, **23**, 379.
[3] Wigglesworth, *J. Expt. Biol.*, 1945, **21**, 97.
[4] Beament, *J. Expt. Biol*, 1945, **21**, 115.
[5] Lees, *Parasitology*, 1946, **37**, 1.

The ability to secrete water in this manner seems to occur sporadically among terrestrial arthropods and has been demonstrated in a few insects, for example, in the mealworm larva,[7] the grasshopper *Chortophaga* [8] and in the prepupa of the flea *Xenopsylla.*[9] Even in the tick it is only the unfed stages that can secrete water: the engorged tick, which obtains an ample supply of water from the ingested blood, usually lacks this power; and so also does the egg.

In these insects the site of entry is unknown. A previous suggestion to the effect that water passes in through the spiracles can be disproved in the tick for uptake occurs normally when the spiracles are covered with an impervious paint (Fig. 1). The cuticle itself must therefore be the site of entry. This is somewhat surprising, for although the pore canals are probably the active agents concerned in transferring water through the main bulk of the cuticle, water will still have to pass in through the wax and polyphenol layers (and possibly the cuticulin layer) of the epicuticle before entering the cytoplasm.

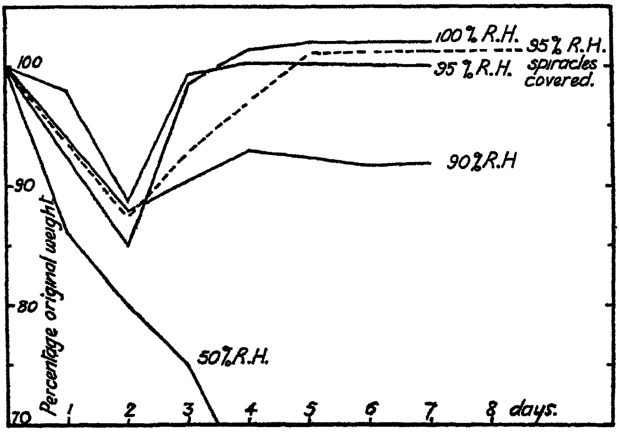

FIG. 1.—Loss and gain of water through the cuticle in *I. ricinus.* Each tick was first desiccated for two days at 50 % R.H. before being exposed at 25° C. to the humidities indicated.

Powers of secretion do not appear to be restricted to any particular region of the epidermis. On the contrary, there are signs of co-ordinated activity among the epidermal cells. Thus, after any given small area of the cuticle has been rubbed with abrasive dust, uptake from a saturated atmosphere may fail completely, although most of the cells still lie beneath normal, undamaged cuticle. After a few days in damp air, recovery takes place and the function is fully restored.

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[6] Krogh, *Proc. Roy. Soc* B, 1946, **133**, 140.

[7] Mellanby, *Proc. Roy. Soc.* B, 1932, **111**, 376.

[8] Ludwig, *Physiol. Zool.*, 1937, **10**, 342.

[9] Edney, *Bull. Entomol. Res.*, 1947, **38**, 263.

The water-content of the blood is regulated as follows. On exposure to a damp atmosphere the desiccated tick at first gains rapidly in weight, then gradually ceases to do so (Fig. 1). As it is possible to show that no water is eliminated by the excretory tubules during prolonged exposures to a humid atmosphere, secretion must also cease when the water-balance has been restored. And this is confirmed by the fact that ticks, when adapted to a saturated atmosphere, lose a little water on exposure to 95 % R.H. before further loss is checked by the development of secretory activity.

This statement implies that active forces will always be at work save when the tick is in saturated air and has all the water it requires. Secretion may therefore be expected to play a significant role in the retention of water at low humidities. This indeed is borne out by the marked increase in cuticular transpiration that takes place when the tick is injured or killed. Moreover, the influence of the active mechanism can also be detected in the physiological effects of ageing.[10] Ticks can survive for many months in damp air without feeding. But although at emergence they attain an equilibrium at a humidity of about 90 % R.H., the equilibrium humidity gradually rises as they age until, in very old individuals, a steady state can only be reached in saturated air. Simultaneously, the resistance to desiccation at humidities below the point of equilibrium declines and, of course, the ability to take up water from slightly unsaturated atmospheres also becomes gradually enfeebled. This is illustrated in Fig. 2 where we plot the weight of a recently moulted female tick which was exposed for 28 weeks to a humidity of 95 % R.H. The average equilibrium humidities of a series of ticks of the same age are shown above. No overall water-loss occurs until, after nearly 24 weeks, the equilibrium humidity passes above 95 % R.H. Then the tick begins to lose water and eventually succumbs to desiccation.

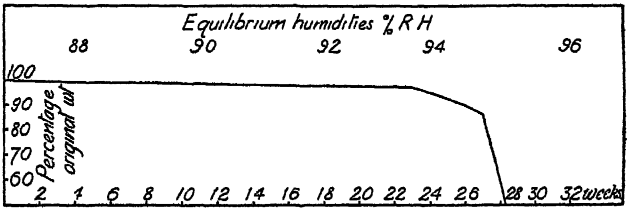

FIG. 2.—Retention of water by a tick (*I. ricinus*) during continuous exposure to a humidity of 95 % R.H. at 25° C.

The efficiency of the active resistance to desiccation is probably determined by the quantity of reserve materials, mainly fats, which are stored in the fat body and other tissues. Thus, if the tick is very active in its movements, the reserves are soon exhausted and the resistance to desiccation falls off rapidly. The tick has then attained a physiological state comparable with that of a more aged but inactive individual.

It will be clear from the foregoing account that the water-exchanges through the cuticle depend on the interplay of passive and active mechanisms. How are these related? With regard to the passage of water *outwards* through the cuticle, both mechanisms evidently combine to retain water with considerable efficiency. Nevertheless, passive retention by the cuticular waxes is of major importance for, as we have mentioned, secretion alone cannot prevent very rapid transpiration after the wax layer has been damaged by abrasion. The presence of this physical barrier therefore reduces the rate of diffusion to a level such that the active mechanism can make a significant contribution towards water conservation.

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[10] Lees, 1948 (unpublished work).

On the other hand, it is an interesting fact that the passage of water *inwards* through the cuticle takes place very easily and appears indeed to be little influenced by the presence of the wax layer. The evidence for this statement is indirect and has been obtained by comparing quantitatively the rate of uptake of water in a range of species selected for the differences in cuticle permeability. Some results with four species are shown in Table I. Each pair of values for evaporation in dry air and uptake in 95 % R.H. or in saturated air refers to the performance of a single unfed tick which had moulted within the previous month.

TABLE I

THE RATE OF PASSAGE OF WATER THROUGH THE CUTICLE OF SEVERAL SPECIES OF TICKS IN MG./SQ CM /24 HR AT 25° C.

	Evaporation in dry air	Uptake at 95 % R H.	Evaporation in dry air	Uptake in saturated air
Ixodes ricinus . . .	5·6	1·9	4·4	4·0
Amblyomma cajennense .	1·2	1·9	1·3	3·1
Rhipicephalus sanguineus .	1·2	2·7	1·6	5·1
Dermacentor andersoni . .	0·5	1·6	0·3	3·0

Although the transpiration rate in dry air differs by a factor of about 10 in the most resistant and most susceptible species, the rate of uptake through a unit area of cuticle is approximately constant in all of them. It would appear therefore that the relative permeability of the cuticle in the direction endo- to epicuticle is not a limiting factor in water-uptake, which may be governed rather by the capacity of the epidermal cells to secrete water at a particular humidity.

This result serves also to throw into relief the notable asymmetry of the water movements through the cuticle. In *I. ricinus* (where the phenomenon is least marked) water passes inwards from saturated air at about the same rate as it passes outwards through the cuticle into dry air. Yet, were the cuticle a simple permeable membrane and the water movements subject only to the laws of diffusion, we should expect from the vapour pressure relations that water-loss would be over 100 times more rapid than water-gain. Of course the tick cuticle is not a simple membrane but instead is made up of successive layers (endocuticle and epicuticle) with strong hydrophilic and lipophilic affinities. And it has been pointed out that the rate of passage of water across such systems may be far from equal in the two directions.[11] Nevertheless, in the present instance it is hardly possible to judge whether the properties of the cuticle are involved, for secretion itself generates " anomalous " water movements through the cuticle.

It is extremely difficult to form an adequate hypothesis of the mechanism of water-gain. A suggestion frequently advanced is that uptake may depend on the hygroscopic properties of the cuticle. This may be the explanation; nevertheless, very large suction forces would have to be developed by the cell in order to withdraw water from the capillary spaces in the cuticle. A capillary, in which water would condense at all humidities above 90 % R.H., would have a diameter of 210 A; and a suction force of about 140 atm. would have to be exerted before any water was removed. The blood osmotic pressure of the tick (9·2 atm. in *I. ricinus*) provides only a small contribution in overcoming this adverse gradient. It is true that in the living tick the retention of water near the equilibrium humidity is determined by the relative humidity of the atmosphere, in much the same way as the water content of a hygroscopic body.[5] Nevertheless, it is equally possible that, diffusion processes apart, a dependence on relative humidity would also characterise other quite different mechanisms.

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[11] Hurst, *Nature*, 1941, 147, 388.

A more instructive approach may be to consider the energy requirements of secretion in relation to the potential energy stores available to the animal. As with many other active processes, the former may perhaps be rather small. Thus the free-energy change involved in transferring water from an atmosphere of 95 % R.H. to one of 99·3 % R.H. amounts to only $1{\cdot}46 \times 10^{-3}$ cal./mg. at 25° C. This minimal figure may be taken as a basis for further calculation. Now the tick takes up water from 95 % R.H. at the rate of 0·2 mg. per day. The energy expenditure would therefore be $2{\cdot}9 \times 10^{-4}$ cal. As 1 mg. of fat yields 9·3 cal. on combustion, the tick would oxidise at least $3{\cdot}1 \times 10^{-5}$ mg. during this period. The various depots in the unfed female (*Ixodes ricinus*) contain about 0·12 mg. of fat at emergence; one day of active secretion would therefore require the minimum utilisation of only one part in 3800 of the stored fat. The conclusion that the secretion of water creates only a negligible demand on the reserve materials (in comparison with the demands of the other metabolic processes) is supported by some experimental evidence. For example, if the tick experiences long periods of secretory activity at 95 % R.H., its survival (which depends on the continued presence of reserves) is not appreciably cut short when it is subsequently returned to saturated air. It may be added as a corollary that in taking up 0·2 mg. of water the tick will gain a relatively large amount of latent heat, namely 0·11 cal. Presumably this is rapidly dissipated to the environment.

The writer is indebted to Dr. J. A. Ramsay, of the Zoological Dept., Cambridge, for estimating the osmotic pressure of tick blood and for assistance in formulating the energy changes involved in secretion; and also to Dr. D. J. Crisp and Mr. J. C. Bevington for advice and discussion.

Summary

The tick cuticle closely resembles that of insects in structure. The endocuticle is penetrated by pore canals arising from the epidermis. And the complex " epicuticle " is made up of successive layers of " cuticulin," polyphenols and wax; in the Argasidæ the latter is covered by an additional layer of cement.

Resistance to evaporation is, in large measure, a *passive* property of the cuticle, conferred by the presence of the waxes in the epicuticle. Impermeability is therefore destroyed when the cuticle is rubbed with an abrasive dust or treated with a wax solvent. The widely dissimilar powers displayed by different species of ticks in resisting desiccation are a reflection of the specific properties of the wax.

But *active* secretion is also of great importance in regulating the passage of water through the cuticle of the living tick. After desiccation, unfed ticks take up water when exposed to high humidities and secrete water into the hæmolymph. This exchange also takes place entirely through the cuticle, where presumably the pore canals and epidermal cells are the active agents.

The newly-emerged tick comes into equilibrium with an atmosphere of about 90 % R.H. Above this humidity it takes up water, ceasing to do so only when the normal water-balance has been restored; below this humidity it loses water by evaporation, but even under these conditions, secretion is responsible for restricting the rate of water-loss. As the tick ages its powers of taking up and actively retaining water gradually decline until finally it can reach equilibrium only in saturated air.

Despite considerable differences in the rate of water-loss in dry atmospheres, the rate of water uptake through the cuticle is nearly constant in all the species examined. In short, although the passive retention of water is greatly influenced by the nature of the wax, active uptake seems to be limited only by the capacity of the epidermal cells to secrete water.

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ASYMMETRICAL BEHAVIOUR OF INSECT CUTICLE IN RELATION TO WATER PERMEABILITY

BY H. HURST

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The evaporation of water through the cuticle of a living insect is mainly influenced by the thin outer epicuticle layer, which contains waxy components. Recent work, notably by Wigglesworth [1] and Beament,[2] indicates that the passage of water through the cuticle is restricted by a thin homogeneous layer of wax on the tanned protein, or cuticulin surface, of the epicuticle. The main impermeable barrier is a thin monolayer of orientated wax molecules at the " epicuticular interface."

Hurst [3] has shown that isolated insect cuticle is more permeable to water in the direction epicuticle→endocuticle than in the reverse direction. The magnitude of this asymmetrical behaviour is in the nature of an " all-or-none " effect, and suggests that contact with liquid water induces a change in structural organisation which extends beneath the epicuticle surface, and is independent of a superficial layer of wax molecules. It has since been found that the phospholipids, lecithin and cephalin, which are highly solvated in water, can participate in the bulk framework of the epicuticle so that the rate of evaporation of water in the direction epicuticle→endocuticle is greatly reduced. Further observations led to the conclusion that the epicuticle is analogous to a porous valve system, the walls of the pores being a restraining flexible network which encloses a laminated lipo-protein. The packing of the lipid components is decreased when the network swells in the presence of liquid water, and increased when the network shrinks. When the network is extended by water, phospholipids can penetrate into the epicuticle, and become adlineated to form a " mixed phase " at the lipo-protein interfaces. The presence of liquid water at the polar interfaces in the laminæ enables the phospholipids to spread and compress the structural lipids so that the permeability of the mixed phase is decreased. In this way the coefficient of asymmetry is decreased.

The object of the present paper is to present relevant experimental evidence in support of this structural pattern, and to show how this pattern is modified in different cuticles.

Evaporation of Water through Isolated Cuticles

The cuticle of the blowfly larva, *Calliphora erythrocephala*, is suitable for studying the rates of evaporation of water in the systems:

(1) water | endocuticle | epicuticle | air
(2) water | epicuticle | endocuticle | air

The cuticle is soft and flexible, and the surface is hydrophilic, and oleophobic in the presence of water. When dry, the surface is wetted by water, or by oil, and no superficial waxy layer is present.

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[1] Wigglesworth, *J. Expt. Biol.*, 1945, **21**, 97.
[2] Beament, *J. Expt. Biol.*, 1945, **21**, 115.
[3] Hurst, *Nature*, 1941, **147**, 388.

The cuticles are removed from the mature larvæ by dissection under water, and attached to micro-osmometers, as shown in Fig. 1 Each osmometer tube has a capacity of about 1 cc.; the dimensions are length 2·6 cm., width 0·23 cm. and internal diameter 0·22 cm. The cuticle is tied to the lower rim of the tube with elastic thread, the tube is then filled with water, and connected to a bent capillary tube (calibrated in divisions of 0·001 cc.) by a piece of thick pressure tubing. The water in the osmometer extends into the capillary tube, and the rate of evaporation of water through the cuticle can be measured directly by the movement of the column in the capillary. The osmometers are mounted on a support and are observed through the glass windows of a constant-temperature chamber, in which the humidity can be adjusted to a given value. In system (1), the endocuticle is in contact with the water in the tube; in (2), the cuticle is reversed. Fig. 2 *a* shows that the rate of evaporation of water r_2 in (2) is much greater than in (1), r_1. The coefficient of asymmetry can be expressed by r_2/r_1. In these particular experiments r_2/r_1 is approximately 70 (20 min.)–20 (60 min.).

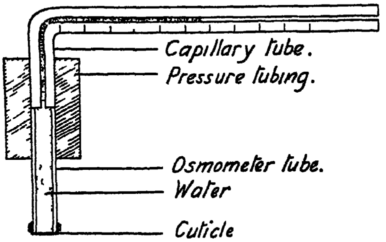

FIG. 1.—Micro-osmometer.

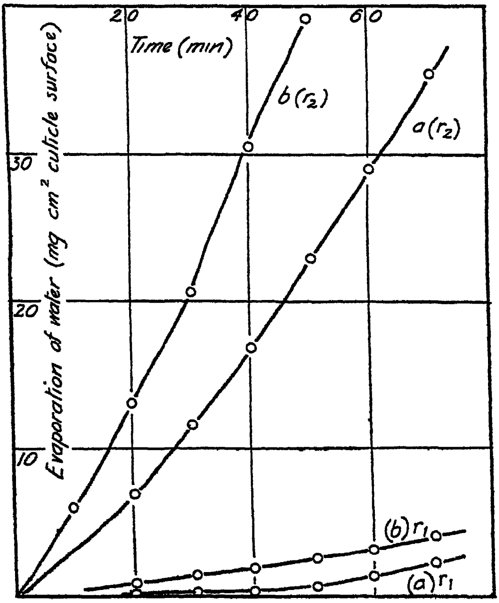

FIG. 2.—Evaporation of water through isolated *Calliphora* cuticles.
r_1 represents system: water | endocuticle | epicuticle | air.
r_2 represents system: water | epicuticle | endocuticle | air.
$a(r_1)$, $a(r_2)$, untreated; $b(r_1)$, $b(r_2)$, chloroform treated.

Action of Chloroform Treatment on the Coefficient of Asymmetry.—If cuticles are used from insects which have been immersed in chloroform for about 30 min., there is a slight increase in r_1, but a relatively greater increase in r_2 (Fig. 2 *b*). From this experiment it may be concluded that chloroform has removed some fat-soluble component from the epicuticle surface or from within the bulk framework. The relative change in r_2 shows that the labile lipid can exert a waterproofing action on the cuticle when the epicuticle is directly in contact with liquid water and the endocuticle with air.

Desiccating Action of Ethyl Alcohol.—The two systems,

(*a*) water | cuticle | air,
(*b*) water | cuticle | ethyl alcohol,

are analogous if air and ethyl alcohol are regarded as dehydrating media which remove water from the outer layers of the cuticle. There is, however, one important difference. In (*a*), it is possible that the outer protective layers contain water vapour. In (*b*), this possibility is precluded owing to the presence of mutually miscible liquid phases on opposite sides of the membrane. It is of interest, therefore, to see whether the cuticle still shows asymmetrical behaviour when the dehydrating medium is alcohol.

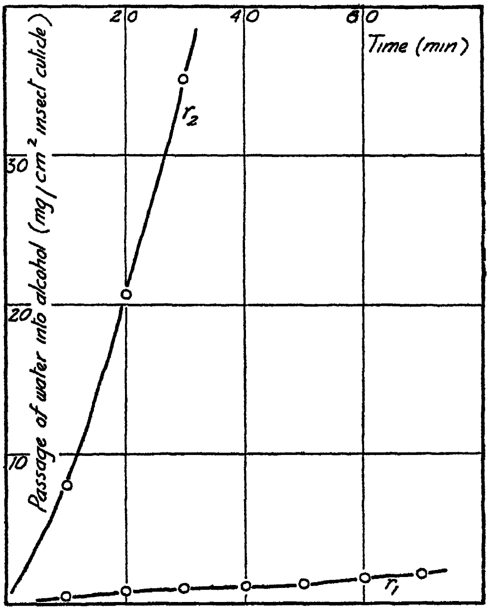

FIG. 3.—Desiccating action of ethyl alcohol.
r_1 represents system: water | endocuticle | epicuticle | alcohol.
r_2 represents system: water | epicuticle | endocuticle | alcohol.

Isolated cuticles of *Calliphora* are attached to osmometers filled with water and the exposed surfaces immersed in ethyl alcohol. The systems can be represented thus:

(1) water | endocuticle | epicuticle | ethyl alcohol.
(2) water | epicuticle | endocuticle | ethyl alcohol.

Since two liquid phases are present on opposite sides of the cuticle, a change in volume of the water phase represents the difference between the rates of flow of water and alcohol in opposite directions across the membranes. Some information about (1) can be deduced from the behaviour of the living insect when immersed in ethyl alcohol. The insect survives, showing that alcohol does not penetrate the cuticle in significant quantities, even after an hour. Since there is no appreciable loss in weight, it can be concluded that water does not pass from the insect into the alcohol. These effects are consistent with the maintenance of a relatively constant volume in the osmometer in (1) (Fig. 3). The decrease in volume in (2) is due to the flow of water into the alcohol phase.

The results correspond closely with those for the evaporation of water through similar cuticle systems. It would appear that there is some valve mechanism in the epicuticle which closes either by the reduction in hydration of the epicuticle, or by the action of fat-soluble lipids in the epicuticle framework. These lipids must be relatively mobile, since they are displaced by chloroform.

The Association between the Epicuticular Lipids and Proteins

Wigglesworth [4] has shown that the epicuticle is secreted as a thin hydrophilic protein membrane, which becomes tanned and impregnated with lipids. Pryor [5] has demonstrated that the tanning of insect cuticle during the natural hardening process involves the combination of an *o*-quinone with the basic amino or imino groups of the protein side-chains. The introduction of aromatic cross-linkages into the protein fabric results in a decrease in hydration, flexibility, and the cuticle darkens. This process is analogous to the tanning and hardening of gelatin by *p*-benzoquinone. In the insect cuticle, however, the *o*-quinone is formed *in situ* from the oxidation of a polyphenol (structurally related to catechol) by a phenoloxidase which is present in the cuticle. Both the enzyme and the substrate are secreted into the cuticle before hardening takes place.

Hardening takes place after a moult, when the new cuticle is soft. This occurs in *Tenebrio* larvæ, and in *Rhodnius*. In blowfly larvæ, however, the hardening takes place at pupation at the end of larval life. In the feeding larva, the cuticle is white, soft and flexible, but the actual cuticulin framework of the epicuticle is extremely resistant to the action of strong acids, such as HCl or HNO_3. The polyphenoloxidase and polyphenol are absent at this stage, yet when the cuticulin layer is warmed in HNO_3 and $KClO_3$, oily droplets are produced, in a similar way to the appearance of droplets from quinone-tanned cast skins of *Rhodnius*.[6] These observations suggest that the chemical stability of the cuticulin layer is not necessarily dependent on a tanning process, but on an extremely stable association between the lipids and structural proteins. A clue to the nature of this association is given by the following experiments.

When an insect is immersed in a solution of *p*-benzoquinone in a fat solvent, the conditions which exist at the cuticle surface may be represented by the system :

	Endocuticle	*Epicuticle*	*Substrate*
blood	water	lipids proteins	fat solvent *p*-benzoquinone

At the epicuticle-substrate interface there is a competition between the lipids and the *p*-benzoquinone for the basic groups of the protein. If the lipids are displaced from the protein by the fat solvent, the protein can combine with the quinone. The degree of cuticle tanning, therefore, is an indication of the extent of protein delipidation, provided that the fat solvent itself does not block access of the quinone to the protein. Moreover, if the storage capacity of the fat solvent for water is large, delipidation of the protein will be accompanied by the passage of water from the cuticle into the substrate. For a range of structurally related fat solvents, such as the homologous series of normal primary alcohols, the time taken for paralysis is a sensitive criterion of the rate of penetration of alcohol. The relationships between alcohol uptake, desiccating action and cuticle tanning when mature *Calliphora* larvæ are in contact with alcoholic solutions of *p*-benzoquinone are summarised in Table I.

The following conclusions may be drawn from Table I.

(*a*) As the homologous series of alcohols is ascended, paralysis inception time decreases to a minimum at amyl alcohol (C_5) and then increases (C_5–C_8).[7] A similar relationship exists when the response measured is desiccation. If biological activity is related to the packing or penetration of alcohol at a lipid-protein interface within the epicuticle, it is clear that the lower alcohols fail to penetrate because the hydrocarbon chains are too short to produce the separation of the hydrocarbon chains of the lipid. At butyl alcohol, however, a critical value in the associating force between the alcohol and lipids is attained and the resistance to penetration breaks down, resulting in a sharp rise in activity and desiccating action owing to the separation of the lipid chains.

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[4] Wigglesworth, *Quart. J. Micro. Sci.*, 1933, **76**, 269.
[5] Pryor, *Proc. Roy. Soc. B*, 1940, **128**, 378, 393.
[6] Wigglesworth, *Proc. Roy. Soc. B*, 1947, **134**, 163.
[7] Hurst, *Trans. Faraday Soc.*, 1943, **39**, 390.

TABLE I

RELATIONSHIPS BETWEEN ALCOHOL UPTAKE, DESICCATING ACTION AND CUTICLE TANNING

Alcohol	Paralysis time (min.)	% loss in weight (3 hours)	Relative tanning (45 min.)
C_1 Methyl	81	—	+
C_2 Ethyl	52	—	+
C_3 Propyl	27	1·4	+
C_4 Butyl	6·4	7·6	++++++
C_5 Amyl	2·1	12·2	+++++
C_6 Hexyl	3·9	9·8	+++
C_7 Heptyl	5·6	5·3	++
C_8 Octyl	7·9	4·6	+

Results record average for 5 insects per test: 20° c. Vol. substrate, 20 cc.: 1 % *p*-benzoquinone.

(*b*) Butyl alcohol not only induces a separation of the lipid chains, but disrupts the polar linkages between the lipid and structural protein. In the absence of benzoquinone, the cuticle becomes opaque and appears to be coagulated. In the presence of benzoquinone, the cuticle is tanned.

(*c*) Although biological activity and desiccating action reach a maximum at amyl alcohol, the degree of tanning begins to fall off at butyl alcohol, showing that another factor is beginning to restrict access of benzoquinone. It would appear that, after penetration into the lipid chains, the alcohol competes with the benzoquinone for the polar side-chains of the protein. In other words, the alcohol replaces the more labile lipids which have been displaced from the protein. Amyl alcohol, in fact, exerts a protective action on the proteins, even though its delipidating action is more pronounced than that of butyl alcohol. This is shown by the slower coagulating action and tanning action in the presence of benzoquinone. With the higher homologues, the progressive fall in biological, desiccating, and tanning activity is due to a decrease in the rate of penetration of the lipid chains owing to the increase in mutual adhesion between the hydrocarbon chains of alcohol molecules. This suggests that the lipid-protein " interface " is not strictly analogous to an oil-water interface where the adsorption and adlineation of alcohol increases with chain length. Similar results are obtained in alcoholic solutions of catechol (1 %).

Adsorption of Alcohols at Lipid-protein Interface

The system amyl alcohol-catechol is of special interest because the amyl alcohol apparently increases the initial rate of penetration of catechol to the lipid-protein or lipid-phenoloxidase interface, and then competes with the catechol at the interface. The first effect is due to a separation of the hydrocarbon chains of the lipids, while the second reflects an equilibrium condition after penetration of both reactants has taken place. If an additional component, chloroform, is introduced into the system, it will increase the permeability of the lipid chains, but will not compete with catechol for the basic groups of the protein side-chains. In the system chloroform-alcohol-catechol, therefore, an equilibrium condition will be rapidly attained, and the rate of cuticle tanning indicates the degree of competition between the alcohol and catechol at the lipid-protein interface. Results obtained for homologues within the range C_4–C_{18} are shown in Table II.

It is seen that, when chloroform has increased the permeability of the lipids, maximum inhibition of cuticle tanning occurs at amyl alcohol. It is significant that the higher homologues, C_{14}, C_{16}, C_{18}, which have the physical properties of waxes, do not block the access of catechol to the protein. If we assume that the protein is strongly hydrated so that a liquid water phase is in contact with the chloroform phase, the higher alcohols should become adlineated and packed at the chloroform-water interface. The delipidation of protein by chloroform increases the hydration of the protein components, and the presence of liquid water should increase the asymmetrical field of force which determines the orientation and stability of the adsorbed alcohol monolayer. Since cuticle tanning is not inhibited, the restraining barrier must be localised in the bound lipids, which are not dispersed by chloroform.

TABLE II

COMPETITION BETWEEN ALCOHOLS AND CATECHOL FOR ADSORPTION AT LIPID-PROTEIN INTERFACE IN THE PRESENCE OF CHLOROFORM

Alcohol component	Relative tanning (30 min)
C_4 Butyl	+++
C_5 Amyl	+
C_6 Hexyl	+++
C_7 Heptyl	++++
C_8 Octyl	++++++
C_{14} Tetradecyl	++++++++
C_{16} Cetyl	++++++++
C_{18} Octadecyl	++++++++
Chloroform—3 % catechol (Control)	++++++++

Chloroform mixtures contain 3 % alcohol, 3 % catechol.
Results record average for 5 insects per test: 20° C.

Stability of Lipo-protein Components of Epicuticle

More critical evidence for the existence of a stable lipo-protein fabric in the epicuticle is obtained with systems of the type: non-polar solvent—short-chain alcohol (C_1–C_3)—catechol.

Kerosene may be used as a non-polar solvent, which is non-toxic to *Calliphora* larvæ, but greatly increases the permeability of the cuticle to ethyl alcohol. An interesting sequence of events can be followed when mature larvæ are immersed in a mixture (2 : 1) of ethyl alcohol and kerosene containing 2 % catechol. The insects survive in the separate solvents for longer than an hour, and are not tanned by catechol in solution. In the mixture, however, the insects die within 10–20 sec., and death is followed by clearly defined changes [8]

(*a*) The insects swell rapidly owing to the penetration of alcohol into the blood.

(*b*) A cloudy zone appears in the substrate near the cuticle surface, and especially at the intersegmental membranes. This is due to the passage of water from the insect resulting in a displacement of kerosene from solution in alcohol.

(*c*) Within 1–2 min. the cuticle turns pink, then red, and the tanning rapidly becomes intensified.

(*d*) In about 5 min. the insect has increased in weight by about 50 %, and bursts, liberating the body fluids and tissues into the substrate.

Similar results are obtained with *p*-benzoquinone as the tanning agent, showing that the lipids exert a similar protective action on the structural proteins and on the associated phenoloxidase. The rate of tanning in the mixed solvent system is many times as rapid as that which takes place when the tanning agent is dissolved in either component. The access of tanning agent clearly depends on a joint action of the solvents on the structural fabric of the epicuticle. The simplest association between kerosene and the lipids is a solvating action leading to the separation of the lipid chains. The mobile short-chain alcohol can now penetrate through the lipid chains and disrupt the polar linkages between the lipids and protein. The alcohol diffuses away from the site of "induced penetration" into the blood, while the kerosene remains immobilised in the lipids. The coagulation of the cuticle appears to be associated with the separation of the polar points of attachment, since kerosene or ethyl alcohol produces no visible change in the texture of the cuticle. The combined action of ethyl alcohol and kerosene is therefore similar to that of butyl, or amyl alcohol, where the essential balance in non-polar and polar associating properties is embodied in the alcohol molecules alone. The insect shrinks in these substrates owing to their limited solubility in the tissue fluids, whereas with the mixed system the rate of access of alcohol is greater than the rate of passage of water through the cuticle.

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[8] Hurst, *Nature*, 1940, **145**, 462.

These effects are independent of the lethal action of the non-polar component in the mixed system. Kerosene may be replaced by more toxic solvents, such as hexane, benzene, toluene, xylene, chlorobenzene, or ether. Ethyl alcohol may be replaced by methyl, or propyl alcohol. It is reasonable to conclude from these experiments that the unit of structure in the epicuticle is a stable lipo-protein, in which stability is independent of tanning by quinone which restricts flexibility, and reduces the degree of hydration. There is strong mutual cohesion between the lipid chains and stable linkages between the polar groups of the lipids and the protein side-chains. The lipo-protein is not directly analogous to a liquid oil-water system, but the high coefficients of asymmetry for the evaporation of water through isolated cuticles show that the lipo-protein must be both stable and extensible to a degree which will permit a wide range of permeability to water. It has been assumed so far that the lipo-protein consists fundamentally of a monolayer of lipid orientated at right angles to the extended protein molecules which are parallel to the cuticle surface. Experiments will now be described to show how a three-dimensional lipo-protein framework can be built up from this simple pattern.

Lateral Diffusion of Catechol through Cuticle

Relationships between membrane structure and permeability are usually based on the flow or diffusion of substances across the membrane. Very little is known of the factors which influence diffusion along a membrane in a direction parallel to the membrane surface. It is known that the actual cuticulin layer of the epicuticle may contain fatty materials which are very strongly bound to the structural proteins, but it is uncertain whether the lipids are uniformly distributed throughout the bulk framework, or show a more specific organisation. There is a wide divergence in the pattern of lipid distribution postulated by different workers. In *Rhodnius*, Wigglesworth[1] and Beament[2] have shown that the protective lipid layer is a thin homogeneous layer of wax, about 0·25μ thick, which is covered by a resistant "cement" layer.[6] The lipids may impregnate the bulk epicuticle framework (Kühnelt[9], Pryor[5]); or the epicuticle may be a double-layer, in which only the outer layer is impregnated with lipid (Richards and Anderson,[10] Dennell[11]). In systems of this kind the barrier to water transpiration through the cuticle may be above, or within the epicuticle framework.

It has been shown that the delipidating action of fat solvents results in the increase in the permeability of the cuticle to water and to catechol or *p*-benzoquinone. The tanned zones indicate the degree of penetration of catechol into the cuticle framework, and a local tanning effect would show that the protein side-chains are more accessible to the tanning substrate in a particular portion of the cuticle. When a mature *Calliphora* larva is treated externally with an aqueous solution of catechol (2 % in phosphate buffer, *p*H 7·4), the cuticle is not tanned because the lipids of the epicuticle restrict the uptake of catechol.[12] If the catechol solution is injected inside the insect (dosage 0·02 cc.), it becomes paralysed, but the cuticle still does not become tanned. When a transverse incision is made through the cuticle, rapid tanning takes place at the cut surface when the insect is immersed in the catechol solution.

[9] Kühnelt, *Zool. Jb. Anat.*, 1928, **50**, 219.

[10] Richards and Anderson, *J. Morphol.*, 1942, **71**. 135.

[11] Dennell, *Proc. Roy. Soc. B*, 1946, **133**, 348

[12] Hurst, *Brit. Med. Bull.*, 1945, **3**, 132.

This experiment is significant in relation to the distribution of lipid in the cuticle framework. If the lipid is localised as a superficial layer on the surface of the epicuticle, access of catechol should be restricted in the direction epicuticle→endocuticle, but not in the reverse direction. Similarly, if the lipid is uniformly distributed throughout the epicuticle framework, access of catechol should be restricted at both surfaces of the cuticle, and at the cut surface. A selective penetration of catechol through the cut surface can only be achieved if the gradient of lipid distribution across the epicuticle framework is discontinous. This discontinuity must be such that the lipids constitute an effective barrier against the loss of water in the direction endocuticle→epicuticle. If the lipids are distributed as a series of leaflets or lamellæ, parallel to the cuticle surface, and orientated with the chains at right-angles to the cuticle surface, passage of water across the cuticle would be restricted, while polyphenol could diffuse readily through the cut surface into the inter-lamellar hydrated protein and associated phenoloxidase. By this lateral diffusion through the membrane, the hydrocarbon chains of the lipid would no longer constitute a barrier to penetration (Fig. 4). A preponderance of lipids in the outer lamellæ, or alternatively, a denser distribution of lamellæ would result in the asymmetrical distribution of lipid which sharply, differentiates the epicuticle from the endocuticle. A stable association between the lipids and structural protein involves both the close packing of the lipid chains and the polar linkages between the lipids and protein side-chains. From X-ray evidence, it is known that the protein molecules are extended parallel to the cuticle surface,[13] [14] and the protection of the polar side-chains of the protein by the lipid could be achieved if the protein occurred in the form of monolayers sandwiched between bimolecular leaflets of lipid. In this system the polar and non-polar side-chains of the protein would be directed on either side of the polypeptide chain towards the polar groups of the lipid. If the polar groups of the protein side-chains, and possibly, the associated polar groups of the lipid are highly hydrated, the epicuticle fabric could have a high storage capacity for water, and could be readily permeable to water along the framework, and impermeable across the framework. The participation of liquid water at the hydrated polar layers is, in fact, essential in relation to the stable orientation of the lipids, and also in relation to the spreading of the more mobile lipid components at the lipid-protein interfaces in the system.

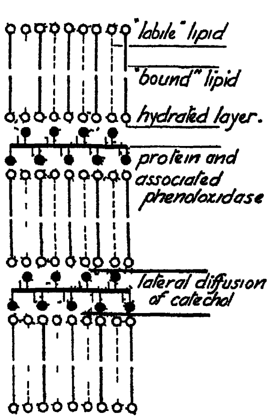
"labile" lipid
"bound" lipid
hydrated layer.
protein and associated phenoloxidase
lateral diffusion of catechol

FIG. 4.—Laminated lipo-protein structure of epicuticle.

From the biophysical point of view, there need be no major difficulty in postulating a structure of this type. The X-ray diffraction studies of Chargaff [15] and co-workers have shown that cephalin forms insoluble "complexes" with basic proteins, such as histone or salmine. The protein molecules are extended between the polar interfaces of the cephalin layers, and there is a strong association between the negative groups of the cephalin and the positive groups of the protein, resulting in a reduction in the hydration of the cephalin. The long diffraction spacing of dry cephalin is increased by 10–15 A in the complexes, according to the type of protein present, suggesting that a single monolayer of protein occurs between successive double layers of lipids This is consistent with the results on the desiccation of insects by fat-solvent treatment. The increase in permeability to water can be reversible, owing to the flexibility of the lipo-protein. This is reflected in the asymmetrical behaviour of the cuticle with respect to the evaporation of water in opposite directions through the cuticle. Since chloroform treatment increases the rate of evaporation in the direction epicuticle→endocuticle more than in the reverse direction, selective directional permeability to water depends primarily on the presence of the bound lipid which is associated with the structural proteins of the epicuticle. The mobile lipids which are displaced from the epicuticle by the chloroform should behave in the following manner.

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[13] Fraenkel and Rudall, *Proc. Roy. Soc. B*, 1940, **129**, 1.

[14] Picken, Pryor and Swann, *Nature*, 1947, **159**, 434.

[15] Chargaff and Ziff, *J. Biol. Chem.*, 1939, **131**, 25.

(1) The association between the mobile lipids and the structural proteins involves a protective action on the basic groups of the protein side-chains.

(2) The distribution of mobile lipids in the epicuticle framework is such that catechol can diffuse laterally through the epicuticle, but not across the epicuticle.

(3) Since the mobile lipids are secreted by the epidermal cells beneath the endocuticle, this layer is permeable to the lipids, which can penetrate in the form of an emulsion.

(4) After penetration into the lamellar framework of the epicuticle, the mobile lipids spread along the lipid-protein interfaces and become adlineated with the bound lipids to form a mixed phase, so that the permeability to water in the direction epicuticle→endocuticle is decreased.

Schmitt and Palmer [16] have shown that when mammalian nerve myelin sheath is dried, the X-ray diffraction pattern reveals three long spacings at 63·5, 44, and 34 A., representing the pattern of sphingomyelin (63·5), cephalin and lecithin (44), and cholesterol (34), as shown in the dry lipids extracted by a benzene-alcohol mixture. There is an equatorial spacing of about 159 A., which is attributed to the presence of protein between the bimolecular leaflets of lipids. In the wet nerve sheath the equatorial long spacing is 184 A., showing that water is present at the polar interfaces between the lipids and the protein, but there is only a single ring at 63·5 A. which is characteristic of sphingomyelin. A similar disappearance of the separate spacings for the lipids occurs when the dried isolated mixed lipids are wetted with water, showing that in the presence of water the lipids are more mobile and can form a mixed phase in which there is adlineation between the hydrocarbon chains. This mobility of the lipids depends on the presence of liquid water at the polar heads of the molecules, and suggests that the phospholipids, lecithin and cephalin are consistent, from the physico-chemical point of view, with the requirements (1)–(4), which have been postulated for the mobile lipids of the epicuticle.

In particular, although the cephalins and lecithins are related structurally the cephalins are more acidic in reaction, owing to the presence of the cholamine group, which is a weaker base than the choline group in the lecithins. It might be expected, therefore, that cephalin should become more strongly associated than lecithin with the basic groups of the protein side-chains in the epicuticle. This is illustrated by the following experiments.

Association of Phospholipids with Epicuticle.—A batch (*a*) of *Calliphora* larvæ, is untreated and used as a control. Other larvæ are injected with (*b*) 0·02 cc. of a 1 % lecithin (Hammarsten) emulsion, and (*c*) 0·02 cc. of a 1 % cephalin (Blix) emulsion in water. (*a*), (*b*), and (*c*) are then placed in a 2 % catechol solution in chloroform. In 3–5 min. the cuticles in (*a*) have reddened. The insects are removed from the chloroform and left in air. The tanning in the cuticles of the controls (*a*) becomes rapidly intensified, and amongst the treated larvæ, (*b*) becomes tanned much more quickly than (*c*), so that the relative order of tanning is (*a*) > (*b*) > (*c*). These results show that in the systems,

(*a*) water	endocuticle	epicuticle	chloroform catechol
(*b*) water lecithin	endocuticle	epicuticle	chloroform catechol
(*c*) water cephalin	endocuticle	epicuticle	chloroform catechol

there is a displacement of lipid from the epicuticle owing to the action of chloroform. This results in an increase in the accessibility of catechol to the exposed basic groups of the protein. In (*b*) and (*c*) lecithin and cephalin pass through the cuticle framework to the site of displacement of labile lipid by the fat solvent. Since the rate of tanning is decreased in the presence of lecithin or cephalin, both components replace the labile lipids which are displaced by chloroform and compete with catechol for the exposed protein. The competition is greater with cephalin than with lecithin, suggesting that there is a combination between the acid phosphoric acid groups of the cephalin and the basic groups of the protein. This type of competition is antagonised by the intra-molecular compensation of positive and negative charges at the cholamine and phosphoric acid groups in the lecithin molecules.

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[16] Schmitt and Palmer, *Cold Spring Harbor Symp. Quant. Biol.*, 1940, **8**, 94.

Action of Phospholipids on Evaporation of Water through Cuticle.—The rates of evaporation of water through isolated cuticles of *Calliphora* larvæ are measured using the osmometer technique which has been described. The osmometer in the control system (*a*) is filled with water. In (*b*) and (*c*) the water is replaced by 1 % lecithin, and 1 % cephalin, respectively. The rates of evaporation of water in the direction endocuticle→epicuticle, and in the reverse direction, are shown in Table III.

TABLE III

EVAPORATION OF WATER THROUGH CUTICLE IN PRESENCE OF LECITHIN AND CEPHALIN

Cuticle system					Rate of evap. (mg./cm.^{2}/hr.)	Coefficient of asymmetry
(*a*)	water	endocuticle	epicuticle	air	1·4	20·6
(*a*)	water	epicuticle	endocuticle	air	28·8	
(*b*)	water lecithin	endocuticle	epicuticle	air	0·82	14·0
(*b*)	water lecithin	epicuticle	endocuticle	air	11·5	
(*c*)	water cephalin	endocuticle	epicuticle	air	0·65	9·1
(*c*)	water cephalin	epicuticle	endocuticle	air	5·9	

Results based on total evaporation during the first hour: 20° C. rel. hum. 50 %.

Lecithin and cephalin restrict the rate of water evaporation in both directions, but mainly in the direction epicuticle→endocuticle, so that the coefficient of asymmetry is reduced. This is consistent with the view that when the epicuticular valve is open and hydrated by contact with liquid water, the phospholipids can penetrate into the valve and spread along the lipid-protein interfaces of the lamellar organisation. When the valve is closed by the dehydrating action of the air, penetration into the bulk epicuticle framework is not a limiting factor in water loss.

From the experimental evidence which has so far been presented, it may be concluded that the passage of water through the cuticle is influenced by a three-dimensional laminated lipo-protein fabric, which is flexible, and hydrated at the polar interfaces (Fig. 4). If the limiting factor in water permeability is the degree of packing between the hydrocarbon chains of the lipids, permeability should decrease if the lamellar fabric is compressed, in the same way as the permeability of a monolayer of long-chain alcohol is reduced by an increase in surface pressure. The crux of the problem is to find some structural restraining network which compresses the epicuticle in the same way as the waxed barriers on a Langmuir trough compress a monolayer. Histological evidence for the existence of a restraining network in the epicuticle is given below.

FIG. 5

(*a*) Optical section through cuticle of *Musca* larva showing mosaic tanned network

(*b*) Diffuse tanned region after chloroform treatment

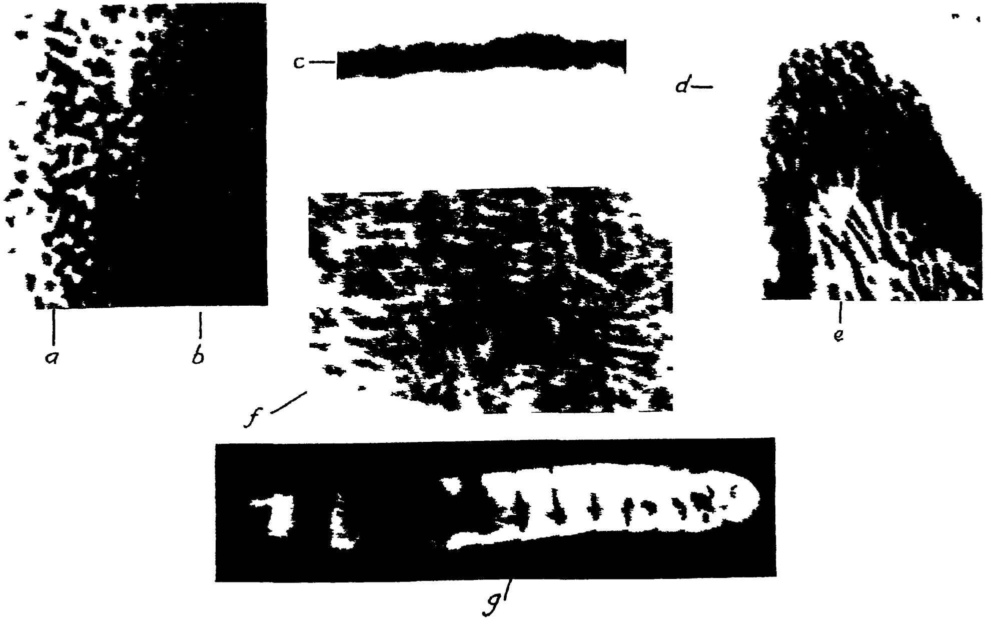
(*c*) Transverse section through cuticle of *Sarcophaga* larva showing epicuticular rods

(*d*) Tangential section through cuticle of *Sarcophaga* larva showing mosaic restraining network (stained acid fuchsin)

(*e*) As in (*d*) showing internal processes of epicuticular rods

(*f*) Transverse section *Sarcophaga* cuticle showing lamellar structure

(*g*) Freshly moulted *Tenebrio* larva showing segmental pattern in posterior segments after rubbing with alumina and immersing in catechol solution



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Mosaic Structure of Epicuticle.—The cuticles of the housefly larva, *Musca domestica*, and the blowfly larva, *Sarcophaga falculata*, are structurally similar to that of *Calliphora* larva. The *Musca* cuticle is thin, and suitable for direct optical examination by transmitted light. *Sarcophaga* cuticle is much thicker, and is suitable for examination in histological sections

An isolated epicuticle layer from a *Musca* cuticle, which has been tanned by the lateral diffusion of catechol through the cut surface, shows a typical mosaic pattern, in which discrete zones are relatively untanned. These zones constitute a mosaic patchwork which is suggestive of a network of fibrils extending across the epicuticle framework[12] (Fig. 5 *a*) After external treatment with chloroform the tanned patches become more extensive, showing that protective lipid is more easily displaced from the lamellar fabric than from the fibrillar network (Fig. 5 *b*).

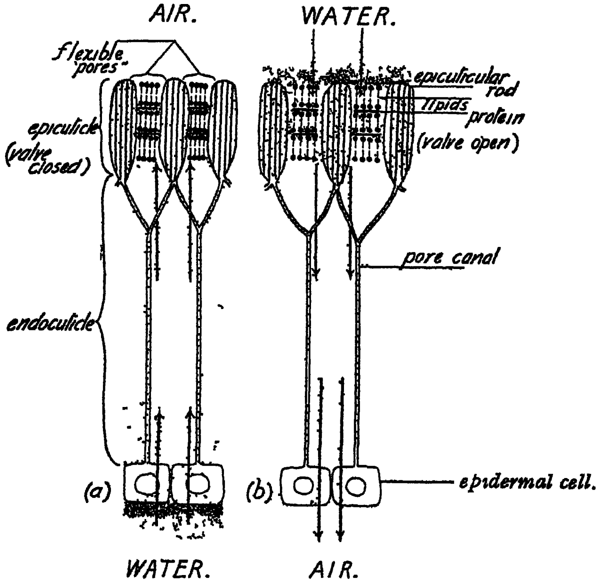

FIG 6 —Structural organisation of epicuticular valve system.
(*a*) Represents system: water | endocuticle | epicuticle | air.
(*b*) Represents system. water | epicuticle | endocuticle | air.

A transverse section through the cuticle of *Sarcophaga* larva reveals peculiar rods, localised in the epicuticle, and roughly orientated radially in relation to the cuticle surface (Fig. 5 *c*). In a tangential section, the epicuticular rods are seen to be part of a fibrous network (Fig. 5 *d*), which becomes abruptly attenuated at the endocuticle, but the processes are continued into this layer (Fig. 5 *e*), and correspond in dimensions and structure with the "pore canals" which usually link the epicuticle with the inner epidermal layer of cells In *Sarcophaga* larva, however, this appears to be of significance during larval growth, for in the mature larva the contents of the canals become solidified[11]

The epicuticular rods in *Sarcophaga* may be analogous to similar structures in the epicuticle of the plastron in *Aphelocheirus*.[17] In this insect the processes appear to be prolonged externally into minute hydrophobic hairs, which retain a film of air when the insect is beneath water so that respiration can take place. A lamellar organisation is clearly seen in the endocuticle framework of *Sarcophaga* (Fig. 5 *f*). It is likely that the lamellar layers in the epicuticle are more compact, although these cannot be distinguished in the particular sections.

If the mosaic network of the epicuticle is regarded as a flexible restraining network, a simplified model of the valve system may be represented as in Fig. 6.

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[17] Thorpe and Crisp, *J. Expt. Biol.*, 1947, **24**, 227.

An expansion of the network opens the valve system, while a contraction closes the valve system.

Mechanism of Asymmetrical Behaviour of Cuticle

When the epicuticle surface is in direct contact with liquid water, a minimum restraint is imposed by the mosaic network on the lamellar lipo-protein framework of the epicuticle. Sebba and Briscoe [18] have shown that a monolayer of a fatty acid or alcohol only become relatively impermeable to the evaporation of water at pressures which are considerably above those at which the film becomes incompressible. It is possible, therefore, that a slight increase in the extension of the network might lead to a considerable increase in permeability if the packing of the lipid chains falls below a critical value. Under these conditions the presence of a relatively small proportion of adsorbed mobile phospholipid could act as a " piston " oil which compresses the chains of the bound lipid. If the restraining network is fully extended, the permeability to water is decreased although the phospholipid component tends to increase the hydration at the polar interfaces of the lipo-protein. This accounts for the reduction in permeability in the direction epicuticle→endocuticle which shows that the phospholipids have penetrated the epicuticle surface and have become adlineated at the lipid-protein interfaces. Sebba and Briscoe have noted that hydrophilic groups in the chain increase the permeability of a monolayer to water. For example, proteins, and the unsaturated acids, oleic and elaidic, show no resistance. Rideal,[19] however, has shown that, when the film is in contact with excess of film-forming agent, oleic acid may reduce evaporation in a vacuum by 52·5 %, at a surface pressure of 29·1 dynes/cm. This system is more related to the condition in the living insect where there is a constant secretion of waxy materials by the epidermal cells. The presence of phospholipids may assist in the transport of wax across the cuticle to the outer layers where a superficial protective film is laid down,[13] but it is also possible that they exert a more dynamic role in relation to change in permeability within the epicuticle lamellar system.

A very simple analogy may be drawn between the epicuticular valve system and a monolayer of long-chain alcohol (e g., octadecyl) enclosed between waxed barriers at an air-water interface. One barrier is fixed and connected by a hair to the movable barrier, which is supported by a torsion wire as in the Langmuir trough. If F represents the pressure exerted by the movable barrier, and F_1 the tension exerted by the hair, the monolayer is subjected to a pressure of $(F + F_1)$. F_1 is at a minimum when the hair is in direct contact with liquid water at the interface, since the degree of extension of the hair is related to the sorption of water. F_1 increases as the hair is brought from the surface of the water into the air, owing to the contraction in length which accompanies desorption of water from the hair. The value of F_1 now depends on the relative humidity of the air and increases with the distance of the hair from the water surface, provided that there is a gradient in humidity under the particular conditions. If the critical surface pressure at which water evaporation through the film is reduced lies between $F + F_1$ (water) and $F + F_1$ (air), the rate of evaporation will be influenced by the hydration of the hair. If the position of the hair is fixed in relation to the water surface, the permeability of the monolayer will increase with humidity, but the rate of evaporation will depend on the humidity gradient extending upwards from the water surface. Since an increase in humidity is associated with a reduction in humidity gradient, the rate of evaporation of water through the monolayer will tend to remain relatively uniform under a wide range of variation in humidity. Similar factors will influence the conservation of water by the epicuticular valve system in the living insect. The essential conditions under which the valve operates reversibly are dependent on (*a*) a flexible restraining network which is extensible by water; (*b*) the presence of liquid water in the lamellar lipid-protein interfaces to ensure mobility of the lipid molecules; (*c*) a degree of restraint in the mosaic network when exposed to air which permits compression of the lipid molecules to a critical value at which water cannot pass between the lipid chains. In the living insect, these conditions are fulfilled in the system,

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[18] Sebba and Briscoe, *J. Chem. Soc.*, 1940, 106.

[19] Rideal, *J. Physic. Chem.*, 1925, 29, 1585.

water | endocuticle | epicuticle | air,

since the epicuticle is spatially separated from the liquid water phase by the endocuticle. In the reversed system,

water | epicuticle | endocuticle | air,

factor (*c*) is no longer effective and the valve system is permeable to water. The epicuticle is thus analogous to a flexible porous membrane, in which the walls of the pores are constituted by a restraining network, and the pores by a laminated lipo-protein enclosed by the mosaic network.

Evaporation of Fat Solvents through Cuticle.—The rates of evaporation of fat solvents through isolated cuticle can be measured with micro-osmometers. The technique is similar to that used for water, but the tubes are filled with fat solvent. Benzene and hexane evaporate through the cuticle of *Calliphora* larvæ very rapidly in the direction epicuticle→endocuticle, but much more slowly in the reverse direction. The coefficients of asymmetry are very high (benzene 15·6, hexane 20·3) and provide critical evidence that (*a*) the restraining network is a lipo-protein which may be extended either by water or fat solvent, and (*b*) the penetration of the fat solvent into the chains of the lipids is restricted by the degree of packing of the chains.

The Role of Wax Layers in the Waterproofing of the Cuticle

If the barrier to the passage of water through the cuticle is a homogeneous layer of wax, the permeability of the bulk cuticle framework should be independent of the position of the wax layer. For example, a layer of wax beneath the endocuticle should restrict the passive transpiration of water in the same way as a layer of wax deposited on the surface of the epicuticle, assuming that the cuticle framework acts merely as a support for the wax layer. These two systems, however, are analogous systems of the type

water | cuticle | air,

in which the epicuticle is in contact with (*a*) air and (*b*) with water. The non-waxy cuticle of *Calliphora* larvæ and the typically waxy cuticle of *Tenebrio* larvæ show similar degrees of asymmetry in relation to the passage of water and volatile fat solvents. Asymmetrical behaviour to water permeation has been confirmed by Beament, using cast skins of 5th-stage *Rhodnius* nymphs.

A superficial wax layer, of the type postulated by Wigglesworth[1] and Beament, would restrict the passive flow of water through the cuticle, but is inconsistent with the selective directional permeability of the cuticle. The experiments on artificial tanning of the cuticle in systems of the type chloroform-alcohol-catechol are of significance in relation to the orientation of the wax molecules in the superficial layer. When the labile lipids are displaced by chloroform, the alcohol can penetrate to the lipid-protein interface and compete with catechol for the basic groups of the protein. There is thus a marked analogy between amyl alcohol and the phospholipids, lecithin and cephalin. The higher alcohols which are typical waxes (e.g., octadecyl) fail to penetrate into the lipid-protein interfaces of the epicuticle, even though the alcohols are dissolved in chloroform. It is unlikely, therefore, that the impermeability of wax films deposited on an artificial membrane framework, such as tanned gelatin, is due to the packing and orientation induced in the lowest layer of molecules in contact with the membrane surface.[1 2] The essential condition for orientation is that a liquid water phase should exist at the membrane-wax interface. It is more probable that the superficial layer of wax at the "epicuticular interface" consists of molecular aggregates in which there is random orientation. Such a layer could exert a protective action on the underlying epicuticular valve mechanism, and modify the sensitivity of the valve according to the particular physiological requirements of the insect.

Desiccating Action of "Inert" Dusts.—Wigglesworth[1] has recently shown that when an insect is rubbed with fine alumina powder, the superficial protective wax layer is abraded, and the insect cuticle becomes more permeable to water. The chief evidence in support of the abrasive mechanism depends on the local staining of the abraded areas by ammoniacal silver hydroxide solution, which is reduced by the exposed polyphenol layer in the cuticle.

The present work has shown that the epicuticle framework permits a selective lateral diffusion of catechol along the membrane, so that the distribution of catechol across the membrane framework is discontinuous. Moreover, since the waterproofing mechanism is a laminated lipo-protein, the exposure of a superficial layer of polyphenol might suggest that a local abrasive action is coincident with, but not necessarily the cause of, an increase in the permeability to water. For example, when a freshly moulted *Tenebrio* larva is rubbed with alumina and immersed in an aqueous solution of catechol, the catechol penetrates into the cuticle at the treated surfaces. But the pattern of tanning which develops is a segmental pattern typical of the natural hardening process (Fig. 5*g*). There is no pattern of local abrasion as revealed by the argentaffin technique. When the *Tenebrio* larva is rubbed or allowed to crawl on moist alumina dust, the cuticle remains relatively impermeable to catechol. Moreover, after 30 min. contact with dry alumina (20° C. ; R.H. 50 %) *Tenebrio* show a loss of 10–15 % in body weight. If the dust is removed from the cuticle by washing in water, and the insect exposed to dry air, it is rapidly desiccated within 2–3 hours, and undergoes a total reduction in weight of 30–40 %. In this condition the segments of the cuticle are telescoped together. A *Tenebrio* larva does not lose weight in moist alumina, or in alumina exposed to air saturated with water vapour. This is not due to the low or negligible gradient in humidity at the epicuticle surface, for when the insect is washed and dried, it still does not become desiccated when exposed to dry air.

It has been shown that the permeability of the epicuticular valve system increases in the presence of liquid water, and this is associated with an increase in mobility of the lipids at the lipid-protein interfaces. The presence of liquid water should therefore favour a mechanical abrasive action of alumina, unless the abrasive action is inhibited by a thin layer of water on the surfaces of the alumina particles. This is unlikely, for a celluloid membrane can be scratched either by dry, or moist alumina. The experiments with lecithin and cephalin have shown that the epicuticle framework is permeable to these components, and the artificial tanning of the cuticle with catechol indicates that the development of a segmental pattern in *Tenebrio* involves a displacement of mobile protective lipid within the epicuticle framework. It follows that there is a functional continuity between the outer lipids associated with the protective waxy layer, and the lipids within the bulk lamellar framework of the epicuticle. The loss of desiccating activity in the presence of water is consistent with the view that water blocks the adsorptive surfaces of the dust particles; but there is an adsorption displacement of lipid from the epicuticle to the dry dust surfaces. The adsorbed lipids are not mobile on the dry dust surfaces, but the degree of displacement is increased by " abrasive " action owing to the presentation of fresh surfaces to the epicuticle. The increase in hydration of the outer epicuticle layers results in an outward displacement of protective lipids within the epicuticle, so that the packing of the chains in the lamellar fabric becomes insufficient to restrict the passage of water through the valve system.

In Fig. 5 *g* the anterior segments of the *Tenebrio* larva show a peculiar local pattern of tanning, which suggests that there are minute patches in the epicuticle which are relatively permeable to catechol. The catechol diffuses through these patches and spreads laterally through the epicuticle framework to form minute tanned rings round each patch. These observations have an important bearing on the natural secretion of polyphenol, for if a freshly moulted larva is treated with ammoniacal silver solution, a similar pattern develops, but each patch stains strongly in the central region, and the stained zone extends internally along a duct to the inner epidermal cells. This pattern only develops after a moult in *Tenebrio* larvæ, or before pupation in blowfly larvæ, and is clearly related to the secretion of polyphenol. A local secretion from a duct into a permeable region of the laminated epicuticle, followed by a lateral diffusion along the hydrated layers would provide an ideal physiological mechanism for ensuring optimum storage and accessibility of polyphenol to the phenoloxidase at a critical stage in the hardening process.

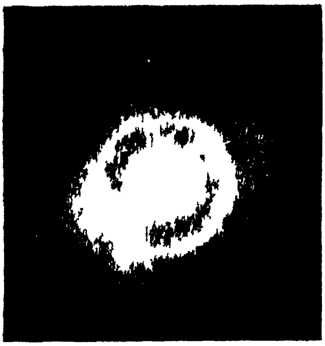

FIG 7 (*a*)—Diffraction pattern *Calliphora* puparial membrane

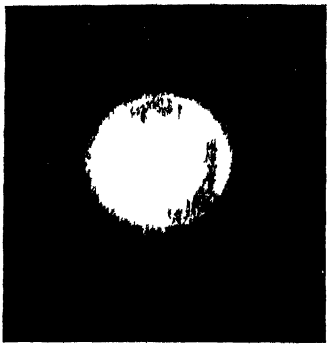

FIG 7 (*b*) Diffraction pattern *Calliphora* puparial membrane after chloroform treatment

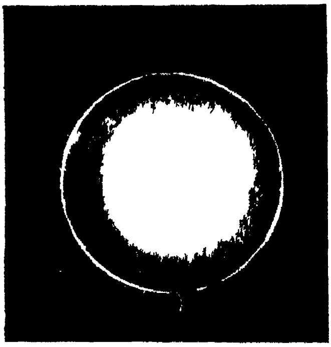

FIG 9 (*a*)—*n*-Fatty acid (c_{16})

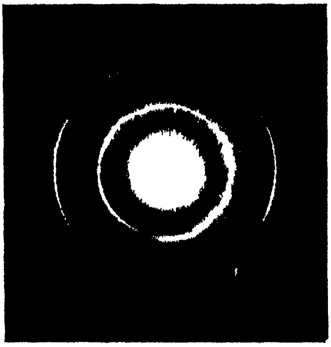

FIG 9 (*b*) *n*-Fatty acid (c[illegible])

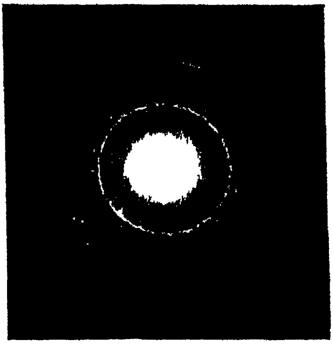

FIG 9 (*c*)—*n*-Fatty acid (c_{34})

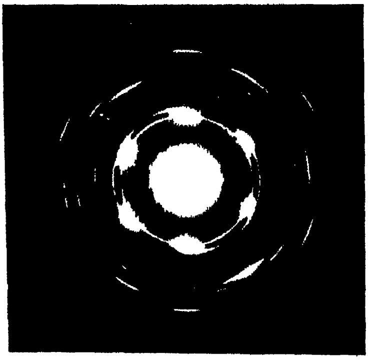

FIG 10—Elaidic acid

To face page 207]

Role of Epicuticular Valve in Active Uptake of Water.—The structure which has been proposed for the epicuticle explains how an insect can conserve essential water, and also how the permeability of the cuticle becomes adjusted to variation in the humidity of the environment. It is known that certain insects can take up water at high humidities approaching saturation, but the mechanism of active " secretion " of water into the blood against a concentration gradient is obscure.[20] The present work has shown that the monolayers of lipid in the laminated epicuticle framework are compressed by a restraining network, and that the valve closes from the outside→inwards owing to the asymmetrical distribution of lipids. The proportion of liquid water in the outer layers of the valve depends on the relative humidity of the air, so that under any particular conditions, a mechanical compression of the restraining network will force water from the outer layers to the inner layers of the epicuticular valve. This will therefore act as a pump under conditions in which there is a supply of energy derived from alternate compression and expansion of the network. The pump will be most effective at high humidities when the outer layers are maximally hydrated.

In the living insect, the cuticle framework is continually being subjected to mechanical compression and extension by the body wall muscles, which are attached to the inner layers of the cuticle. The conditions are such that the epicuticular valve can restrict the passive transpiration of water from the cuticle, modify cuticle permeability according to the change in the environment, and at critical humidities, bring about the active uptake of water by the insect.

Appendix (Added in Proof, *7th June*, 1948)

Electron Diffraction By Cuticle Lipids.—Electron diffraction techniques have been extensively used for studying the orientation of thin films of *n*-paraffins and long-chain fatty acids, but the techniques have so far not been used for natural membrane systems. In order to show that orientated layers of lipids are present within the cuticle framework, it is necessary to obtain diffraction patterns by transmission with the incident beam normal to the surface of the cuticle. If a characteristic pattern is obtained which disappears when the cuticle is treated with a fat solvent, this would suggest that the fatty components are present as a thin superficial layer in which the molecules are orientated in a common direction. If the pattern persists after prolonged contact with a fat solvent, this would show that orientated units of lipids exist within the cuticle and are strongly associated with the structural proteins.

The thin puparial cast skins of blowflies, which are left behind in the puparium after the flies emerge, are about 2–3 μ thick, and when floated on water one surface is seen to be waxy and hydrophobic while the inner surface is hydrophilic. These membranes may be readily mounted on a small circular grid adapted for use with the R.C.A. electron microscope and diffraction unit. When examined with the microscope, no heterogeneous structure is visible at a magnification of 20,000 ×. But the electrons are only slightly absorbed by the membrane, which is somewhat surprising, considering its relative thickness. This observation, however, suggests that some evidence of molecular orientation might be obtained by diffraction of a beam at normal incidence to the cuticle surface. This view is confirmed by the characteristic ring patterns obtained by transmission. By suitable exposure it is possible to distinguish two sharply defined central rings (Fig. 7, *a*) surrounded by three wider rings, which are fainter. This ring system is shown in Fig. 8. From these patterns it may be concluded that

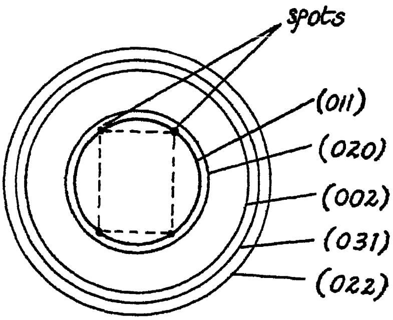

Fig. 8.—Diffraction ring pattern of insect cuticle (*Calliphora* puparial membrane).

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[20] Lees, *J. Expt. Biol.*, 1947, **23**, 397.

the cuticle contains a definite crystal structure in which the molecules are orientated in the same way in relation to the cuticle surface, but otherwise distributed at random in relation to a plane normal to the cuticle surface. The presence of polycrystalline associations is indicated by the spots on the lines.

The pattern persists after the preparation has been treated for 2 hr. in chloroform, but the rings are somewhat sharper, and the spots have mainly disappeared, showing that the fat solvent has not changed the fundamental crystalline structure apart from reducing the size of the crystalline aggregates (Fig. 7 *b*). Any labile lipids removed by the chloroform must either not contribute to the diffraction pattern, or they are associated with the bound lipids in the cuticle, if these fatty components are responsible for the pattern. The pattern disappears after treatment with strong caustic potash, which disrupts the lipo-protein fabric.

A clue to the nature of the orientated molecules is given by the four spots which are clearly seen on the inner ring. (Fig. 8). When joined by lines these spots form a rectangle. The ratio of the lengths of the sides *a* : *b* is approximately 1·5 : 1. This ratio corresponds closely to the unit cell cross-section common to long-chain fatty acids, paraffins and alcohols. Conclusive proof that this type of fatty material is present in orientated form in the framework of the cuticle is provided when the diffraction patterns of the cuticle are compared with the patterns obtained with thin films of collodion containing orientated crystalline fatty acids.

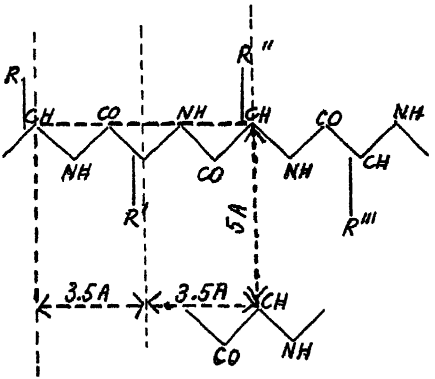

FIG. 11.—Relationship between lipid unit cell and protein chains ('β-keratin' configuration) (base of unit cell heavily dotted).

The collodion fatty-acid membranes are prepared by dissolving 5–10 % fatty acid in a dilute solution of collodion in amyl acetate. When a drop of solution is allowed to fall on a clean water surface, the collodion spreads rapidly to form a thin coherent film, which is only a few hundred A. thick.* This process takes place in less than a second, before the solvent has evaporated, so that the fatty acid is in solution in the collodion-solvent system during the spreading of the film. The polar groups of the fatty acid molecules become directed downwards towards the water surface, and when the solvent has evaporated the minute crystals formed are embedded in the collodion membrane with the axes of the hydrocarbon chains normal to the membrane surface. When these membranes are examined in the same way as with the insect cuticle, typical sharp ring patterns are obtained, which vary according to the fatty acid present (Fig. 9). Some interesting conclusions may be drawn from a preliminary comparison of the ring patterns with those of the insect cuticle.

(1) A central ring of the same diameter is present in the patterns of insect cuticle, fatty acids (C_{16}), (C_{18}), (C_{34}). By standardisation with a crystalline gold film deposited on collodion, the spacing responsible for this ring is seen to be equivalent to *ca* 4·15 A. An outer ring representing a spacing of *ca* 2·44 A. is also present. The ring system of C_{34} corresponds almost exactly to that of the insect cuticle in relation to the intensities and distributions of the rings. The sharp ring patterns of discrete spots reveal the presence of orientated polycrystalline layers in which the unit cells are grouped in random (001) orientation with respect to the plane of the membrane surface.

(2) A membrane containing the unsaturated elaidic acid (C_{18}) shows a well defined series of rings in which there is a pseudo-hexagonal arrangement typical of *n*-paraffins, fatty acids, and fatty acid esters. The lines are continuous,

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* Collodion alone gives a diffuse ring pattern which can readily be distinguished from the sharp ring pattern of the fatty acids.

suggesting a more random orientation of separate molecules, which are similarly orientated but more mobile than those in the *n*-fatty acid members (Fig. 10). The bright diffuse spots on the 4·15 A. ring form a rectangle, in which the ratio of the lengths of the sides is similar to that formed by the spots on the diffraction pattern of insect cuticle. This suggests that the unit cell of the fatty components in the cuticle is analogous to the orthorhombic unit cells of *n*-paraffins and fatty acids.*[21][22] Striking confirmation of this view is obtained from a comparison of the observed spacings with the calculated diffractions from an orthorhombic *n*-paraffin unit cell (where $a = 7{\cdot}45$ A., $b = 4{\cdot}97$ A., and c is twice the length of the molecule and normal to the membrane surface) (Table I). The diffractions represent successive orders of diffractions by alternate carbon-carbon spacings of 2·54 A. in the zigzag hydrocarbon chains, which are normal to the surface and in all azimuths in relation to the incident beam.

The radii of the diffraction rings, which have Laue indices of the form *hkO*, are given by the relationship

$$r = \lambda L\sqrt{\left(\frac{h^2}{a^2} + \frac{k^2}{b^2}\right)}$$

where r is the radius of the ring, λ the wave-length of the electron beam, L the distance between the specimen and the photographic plate, and h and k are Laue indices relative to the a- and b- axes respectively. In the calculated spacings $a = 7{\cdot}45$ A. and $b = 4{\cdot}97$ A.

TABLE I

RELATIONSHIPS BETWEEN CALCULATED SPACINGS FOR AN ORTHORHOMBIC *n*-PARAFFIN LATTICE, AND OBSERVED SPACINGS FOR FATTY ACIDS, AND LIPIDS OF INSECT CUTICLE (PUPARIAL MEMBRANE OF *Calliphora*)

Layer line order	Laue indices	Spacing (A.)			
		(Calculated)	(Observed)		
		n-paraffin	elaidic acid	C_{34} acid	Cuticle
1	010	7·45	7·35	—	—
1	001	4·97	4·95	—	—
1, 2 ..	011	4·13	4·15	4·12	4·15
1, 2 ..	020	3·73	3·65	3·68	3·69
1	021	2·98	2·94	2·94	—
2	002	2·48	2·44	2·43	2·43
1	012	2·36	2·31	2·33	—
1, 2 ..	031	2·22	2·18	2·20	2·18
1	022	2·06	2·03	2·03	2·05
1	032	1·76	1·73	—	—
1	023	1·51	1·49	—	—

(50 kv.; 200–400 μa. beam current; lattice spacing of gold standard, $a = 4{\cdot}07$ A.)

The identity of the crystal structures is shown by the coincidence in the spacings between the (011), (020), (002), (031), and (022) planes, which is consistent with the (001) orientation of the unit cells. Adopting the observed spacings for elaidic acid as a standard, the dimensions of the unit lipid cell in the cuticle are $a = 7{\cdot}35$ A., $b = 4{\cdot}95$ A. The ratio of these dimensions is 1·49 : 1, which coincides almost exactly with the ratio of 1·5 : 1 for the length and width of the rectangle formed by the spots on the diffraction ring of the (011) plane in the elaidic acid and cuticle patterns. This confirms the view that the lipids in the cuticle are in the form of crystal patterns orientated at right-angles to the cuticle surface and probably associated in layers between the structural protein fibrils. The dimensions of the cells correspond to the distance between three polypeptide groups on a protein chain in the β-keratin configuration, (7 A.) and the spacing apart of two chains (4·5—5 A.). The lipids may be arranged in bimolecular units, or in multilayer formation, with the unit cells aligned with the extended proteins, and probably associated with the polar groups of the side chains to form lipo-protein complexes (Fig. 11). Association between the lipids and structural proteins may also occur between the hydrocarbon chains and the non-polar side chains of the protein.

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[21] Germer and Storks, *J. Chem. Physics*, 1938, **6**, 280.
[22] Cowley, *Trans. Faraday Soc.*, 1948, **44**, 60.

I am indebted to R. G. Allen, of the Cavendish laboratory and Mr. Mentor, of the Physical Chemistry Dept., Cambridge, for helpful advice and discussion on this section of the work ; and to Mr. G. R. Crowe for technical assistance.)

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THE WATER-PROTECTING PROPERTIES OF INSECT HAIRS

BY D. J. CRISP AND W. H. THORPE

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The terms " waterproofing " and " water-protecting " have been applied to different processes, and it will be useful to distinguish them clearly. Sub-aerial plants and animals are commonly protected against liquid water which might otherwise block the pores, spiracles or stomata through which gas exchange takes place. Aquatic birds are similarly protected for purposes of buoyancy and heat retention. This protection usually takes the form of hydrofuge hairs, scales or other structures which offer a purely physical barrier to liquid water and are permeable to its vapour. The second type of waterproofing structure refers to a barrier impermeable to molecular water whether in liquid or vapour form, and is commonly found when organisms live under conditions of low humidity or drought so that water conservation by means of a covering of wax or lipo-protein is of value.

The subject matter of this paper deals with some highly specialised devices of the first type which enable certain wholely aquatic insects to retain a thin film of air on the surface of their bodies. This film functions as a gill, allowing oxygen to be absorbed from the surrounding water and passed directly through the air tubes (tracheæ) into the tissues of the insect.

Pressure Differences Sustained by the Air Space

The gas content of a bubble or film of air carried by an aquatic insect will change continuously, due to :

(*a*) removal of oxygen at the end of the tracheæ by respiring tissues ;
(*b*) diffusion of carbon dioxide from the tissues ;
(*c*) diffusion of oxygen and nitrogen between the air space and the surrounding water.

To a good approximation the time factor for diffusion within the gas space may be neglected, the whole space being assumed to be of uniform constitution. Similarly, the partial pressure of carbon dioxide may be neglected as it is so rapidly dissolved away by the surrounding water.

It is useful here to introduce the concept of an *invasion coefficient*,[1] i, defined as the quantity of gas crossing unit area of gas-liquid interface under unit difference of gas tension between the two phases. The barrier to diffusion is not the interfacial layer, but the diffusion shells of liquid bounding the surface[2]; hence the value of i depends not only on the permeability of the liquid to the gas, but also on the state of convection currents near the surface. It is not, therefore, a well-defined physical entity but has, nevertheless, a definite value for fixed conditions of convection, while the ratio of invasion coefficients of different gases at a given interface will be proportional to their permeabilities in the liquid. Hence that of oxygen in water (i_O), will be about twice that of nitrogen (i_N).

We may therefore describe the changes in gas content of such an air space by

$$\frac{dO}{dt} = Ai_O(t_O - p_O) - q \quad . \quad . \quad . \quad . \quad (1)$$

$$\frac{dN}{dt} = Ai_N(t_N - p_N) \quad . \quad . \quad . \quad . \quad (2)$$

where O and N are the amounts of oxygen and nitrogen in the air space (in cc. at atm. pressure), q is the rate of oxygen uptake, A the area of gas-water surface, and p_O, p_N; t_O, t_N; the pressures and tensions (in atm.) of oxygen and nitrogen respectively in the air space and in the surrounding water.

Two possible conditions may now be applied to the air space.

(*a*) A steady pressure P is maintained on the air space,

$$\text{then} \quad p_O + p_N = P \quad . \quad . \quad . \quad . \quad (3)$$

$$\text{and} \quad \frac{dV}{dt} = \frac{dO}{dt} + \frac{dN}{dt} \quad . \quad . \quad . \quad . \quad (4)$$

where V is the volume of gas present.

The solution of these equations is complex, and need not be considered here. We may note, however, that if we write $P = (1 + h\rho g)$, where $h\rho g$ refers to the pressure increment with depth h, and assume $t_O + t_N = \text{or} < 1$ (i.e., the water is not supersaturated).

$$\frac{dV}{dt} = \text{or} < \underbrace{Ai_O(t_O - p_O) - q}_{\text{Net increase in Oxygen}} - \underbrace{Ai_N(t_O - p_O + h\rho g)}_{\text{Loss of Nitrogen}}$$

$$\text{or} \quad \frac{dV}{dt} = \text{or} < A(i_O - i_N)(t_O - p_O) - q - Ai_N h\rho g \quad . \quad (5)$$

Since $(i_O - i_N)$, q, and $Ai_N h\rho g$ are positive $\frac{dV}{dt}$ will be negative when $p_O > t_O$. When $p_O < t_O$, the sign of $\frac{dV}{dt}$ might at first be positive, but as the net rate of increase in oxygen content O must always exceed the rate of increase in volume V, $p_O \left(= \frac{O}{V}\right)$ must increase, approaching the value t_O, and thus eventually making $\frac{dV}{dt}$ negative. When h is small, eqn. (1), (5) show that if $q > Ai_O t_O$, oxygen is continuously lost, hence p_O must fall to zero; but if $q < Ai_O t_O$, then V falls to zero. In either case this leads to failure of respiration unless the insect can renew its store of air,[3] and this type of air space may aptly be called an "air-store."

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[1] Krogh, *Skand. Arch. Physiol.*, 1910, **20**, 259.
[2] Krogh, *J. Physiol.*, 1919, **52**, 391.
[3] Ege, *Z. allg. Physiol.*, 1918, **17**, 81.

(*b*) The air space is maintained at constant volume,

Then $\frac{dV}{dt} = 0$ and $\frac{dN}{dt}$ and $\frac{dO}{dt}$ are independent,

giving
$$\frac{dO}{dt} = V\frac{dp_O}{dt} = Ai_O(t_O - p_O) - q.$$

Solving this and applying boundary conditions,

$$p_O = \left(t_O - \frac{q}{Ai_O}\right) + \left(p_{O\,1} - t_O + \frac{q}{Ai_O}\right) e^{-\frac{Ai_Ot}{V}} \quad . \quad (6)$$

and similarly
$$p_N = t_N + (p_{N_1} - t_N)\, e^{-\frac{Ai_Nt}{V}} \quad . \quad . \quad . \quad (7)$$

where p_{O_1} and p_{N_1} are the initial partial pressures of oxygen and nitrogen. Calculation of the time constants shows that equilibration is very rapid, being usually of the order of a few seconds.[4] In the steady state ($t = \infty$)

$$p_O = t_O - \frac{q}{Ai_O} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

$$p_N = t_N \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Thus a pressure difference Δp is set up across the walls of the air space,

$$\Delta p = P - (p_O + p_N) = 1 + h\rho g - (t_O + t_N) + \frac{q}{Ai_O} \quad . \quad (10)$$

while provided $Ai_Ot_O > q$, a steady flow of oxygen may be maintained sufficient for respiration without the animal requiring to visit the surface.

This type of respiration is characterised by an air space possessing:

(i) large surface area/oxygen requirement ($Ai_Ot_O > q$);
(ii) small volume, since it does not act as a store of oxygen;
(iii) a mechanism of hydrofuge hairs or scales to prevent ingress of water and maintain the pressure difference Δp caused by the respiration rate and the degree of unsaturation of the water (eqn. (10)).

We have termed this kind of respiratory organ the "plastron" and the process "plastron respiration," as it is fundamentally distinct from the air-store described under (*a*) above.

We shall next consider the diffusion within the plastron and the restrictions it imposes upon its structure.

Theory of Diffusion in the Plastron

Fig. 1 shows diagrammatically the essential features in the operation of the plastron; the vertical arrows represent invasion of oxygen across the planes XOY, X'O'Y' from a steady tension t_O in the outside medium into the plastron space at a partial pressure of oxygen p_O. The value $t_O - p_O$ is called Δp_O*, and it is clear that both p_O and $|\Delta p_O|$ must fall along $\overrightarrow{XO}$ and $\overrightarrow{X'O'}$ in order to allow diffusion of oxygen (as indicated by horizontal arrows) towards the spiracles, represented here as a groove YY'OO'ZZ'. It is reasonable to assume in the insects we have studied that, to a first approximation, diffusion occurs entirely in the direction XO and X'O'; this reduces the problem to two dimensions and the relation is found to be[5]

$$\frac{d^2(\Delta p_O)}{dx^2} - n^2\,\Delta p_O = 0 \quad . \quad . \quad . \quad . \quad . \quad (11)$$

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[4] Thorpe and Crisp, *J. Expt. Biol.*, 1947, **24**, 310.

[5] Thorpe and Crisp, *J. Expt. Biol.*, 1947, **24**, 270.

* This was called simply p in a previous publication (ref. [5], Appendix I) and the solution was given a different form.

where $n^2 = \frac{i_O}{Dh}$, h being the thickness of the plastron (Fig. 1) and D the effective diffusion constant of oxygen within the plastron space.

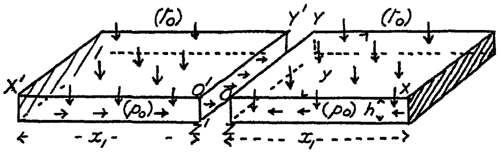

FIG 1 —Diagrammatic representation of diffusion into and through the plastron
Vertical arrows—Invasion of oxygen across the air-water boundary.
Horizontal arrows—Gaseous diffusion of oxygen within the plastron space

If q is the total oxygen uptake, the diffusion across one side of the groove is $\frac{q}{2}$, hence at the planes YOZ and Y′O′Z′ where $x = 0$,

$$\frac{q}{2} = -yhD\left(\frac{dp_O}{dx}\right)_{x\ 0}$$

Since $dp_O = -d(\Delta p_O)$ we have as a first boundary condition to eqn. (11)

$$\left(\frac{d(\Delta p_O)}{dx}\right)_{x=0} = \frac{q}{2yhD}$$

and as a second, since x_1 is the limit of the plastron,

$$\left(\frac{d(\Delta p_O)}{dx}\right)_{x=x_1} = 0$$

The solution is *

$$\Delta p_O = (\Delta p_O)_m\,[Me^{nx} + Ne^{-nx}] \quad . \quad . \quad . \quad (12)$$

$$\text{where } (\Delta p_O)_m = \frac{q}{2x_1 y i_O},\ M = \frac{nx_1}{(e^{2nx_1} - 1)}$$

$$N = \frac{ne^{2nx_1}}{(e^{2nx_1} - 1)}$$

The significance of $(\Delta p_O)_m$ is that it is the mean pressure drop across the plastron since $2x_1y$ is the plastron area. The pressure drop at the outer edges (X,X′) is less than $(\Delta p_O)_m$:

$$(\Delta p_O)_{x=x_1} = (\Delta p_O)_m\,[nx_1/\sinh(nx_1)] \quad . \quad . \quad (13)$$

While at the spiracular openings or grooves (YOZ, Y′O′Z′) it is greater:

$$(\Delta p_O)_{x=0} = (\Delta p_O)_m\,[nx_1/\tanh(nx_1)] \quad . \quad . \quad (14)$$

Now it is this drop in partial pressure between the outside medium and the spiracle that is important to the organism, and must be kept as low as possible for maximum respiratory efficiency. It will be seen from eqn. (12) that while the mean drop in partial pressure depends on the respiration rate, the plastron area, and i_O, the *shape* of the distribution of partial pressures within the plastron depends solely on the function $nx_1 = \sqrt{\frac{i_O x_1^2}{Dh}}$. It follows that in order to reduce $(\Delta p_O)_{x=0}$ for a given value of $(\Delta p_O)_m$, nx_1 must be small; for if $nx_1 = 0$ the $\Delta p_O - x$ curve is flat and $(\Delta p_O)_{x=0}$ is minimal, invasion operating equally over the whole plastron area (see Fig. 2); but if nx_1 exceeds, say, unity then (Δp_O) decreases considerably towards the spiracles and only part of the plastron is efficiently used.

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* See footnote p. 212.

However nx_1 can only be reduced by increasing D and h, as any decrease in i_0 or x_1 would have a direct influence in lowering the mean pressure of the plastron below its surroundings. Fig. 2 gives a series of curves showing the influence of nx_1, and it will be seen that curve 1, based on observations on the natural plastron of the insect *Aphelocheirus*, represents a fairly efficient system. It may be mentioned here that no evidence of secretory activity exists either in the plastron or in related structures as suggested by Szabo-Patay,[6] diffusion being adequate for the necessary oxygen transfer.[5]

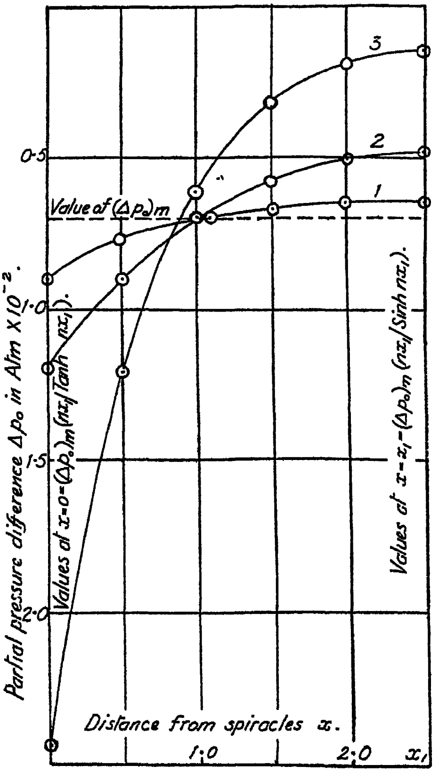

FIG. 2.—Values of oxygen tension difference (Δp_0) between plastron space and medium calculated from eqn. (12) using the following constants:

$D = 0{\cdot}1$ cm.^{2}/sec. (less than the value 0·18 for oxygen in air owing to the space occupied by hairs).

$i_0 = 4 \times 10^{-4}$ (less than Ege's value of $4{\cdot}8 \times 10^{-4}$ owing to reduction of gas-liquid surface by hairs).

$x_1 = 0{\cdot}25$ cm., $y = 1{\cdot}2$ cm. (two lines of spiracles each 0·6 cm. long).

$q = 6 \times 10^{-3}$ cc. oxygen at N.T.P. per hour.

$h = 5 \times 10^{-4}$ cm. (Curve 1); 1×10^{-4} cm. (Curve 2); $0{\cdot}2 \times 10^{-4}$ cm. (Curve 3).

The uptake by the plastron at any x value is proportional to Δp_0.

We shall now consider the different ways in which the plastron might be constructed in order to withstand excess pressure at the gas-water interface.

Theory of Water Proofing by Surface Forces

Let θ be the angle of contact between a hair surface and water, and γ the surface tension of water. The relations below then follow from the general equation

$$\Delta p \,.\, a \,.\, dx + \gamma \cos\theta \,.\, n \,.\, dS = 0 \qquad . \quad . \quad . \quad (15)$$

where dS is the element of area wetted on each of n hairs when an area a of free water surface moves through a distance dx under the pressure Δp.

Δp is the excess pressure on the *water* side of the interface so that water protection is indicated by a positive value for Δp.*

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[6] Szabo-Patay, *J. Ann. Mus. Nat. Hungary*, 1924, **21**, 33.

* This convention was not strictly adhered to in an earlier paper where the negative signs in eqn. (16), (17) and (18) were omitted.

(*a*) If the plastron is maintained by vertical hairs of circular cross-section, of radius r, then

$$\Delta p = -\frac{2\pi r}{l^2 - \pi r^2} \cdot \gamma \cos \theta \qquad . \quad . \quad . \quad (16)$$

where l is the characteristic distance between the hairs defined by $l =$ (number of hairs per sq. cm.)$^{-\frac{1}{2}}$. If the hairs are disposed as a pattern of squares, l will be the actual distance separating them.

(*b*) If the hairs are inclined at an angle α to the horizontal,

$$\Delta p = -\frac{2\pi r \operatorname{cosec} \alpha}{l^2 - \pi r^2 \operatorname{cosec} \alpha} \cdot \gamma \cos \theta \qquad . \quad . \quad (17)$$

though it is clear that the angle α is limited since eventually the hairs would touch one another.

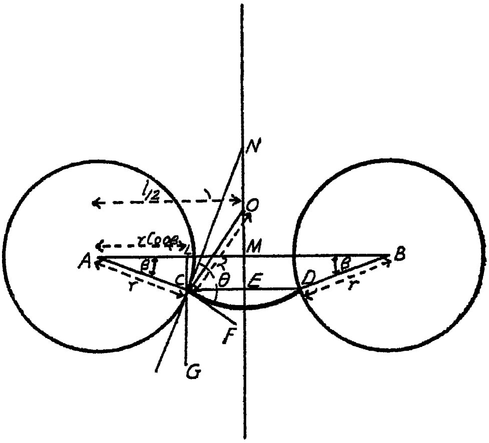

FIG 3—Sectional view of two hairs lying horizontally at the interface, showing the meniscus (arc CD) making contact angle θ with each of the hairs The aqueous phase lies above the meniscus.

(*c*) The hairs may be arranged as a horizontal array, a cross-section of two such hairs of circular cross-section is shown in Fig. 3. The excess pressure is best calculated from the radius of curvature (R) of the cylindrical bubble surface arc CD.

$$\Delta p = \frac{\gamma}{R}$$

M is the mid point of AB which joins the centres of two hairs, hence AM $= l/2$. AC, BD are the radii of cross-section of the hairs ($= r$) and CN, CF, are respectively the tangents to the hair and to the water surface at the point of contact; the lines EMON and CL are drawn perpendicular to AB. Now, by reason of symmetry, since $\hat{CAB} = \hat{ABD} = \beta$; OC = OD = R; OC being at right angles to the tangent CF; and CE = ED = LM $= l/2 - r \cos \beta$. Further, $\hat{LCN} = \beta$ and $\hat{GCF} = 180° - \theta - \beta$.

By placing $\hat{FCO}$ over $\hat{GCE}$, it is clear that $\hat{GCF} = \hat{OCE} = 180° - \theta - \beta$.

But CE $= \text{R} \cos \hat{OCE} = R \cos (180° - \theta - \beta)$

$$= -R \cos (\theta + \beta) = \frac{l}{2} - r \cos \beta$$

$$\therefore \; R = -\frac{l/2 - r \cos \beta}{\cos (\theta + \beta)} \; . \quad \text{Hence } \Delta p = -\frac{\gamma \cos (\theta + \beta)}{l/2 - r \cos \beta} \quad . \quad (18)$$

By differentiation, the critical value of Δp for $\frac{d\Delta p}{d\beta} = 0$ is found to be

$$\frac{\sin (\theta + \beta)}{\sin \theta} = \frac{2r}{l} \qquad . \quad . \quad . \quad . \quad . \quad (19)$$

There are in general two values of β satisfying (19); one gives Δp its maximum positive value, the other its maximum negative value. Here we are concerned with the former for which β lies between 0 and + 180° though in practice β may not exceed 90° without the menisci becoming confluent. This range of β (0 to $+ 90°$) corresponds to a range of θ between $+ 180°$ and $0°$, hence Δp can be positive for all values of θ.

The following conclusions may be drawn from the above relations.

1. For simple hairs, vertical or inclined, water protection is only possible when $\theta > 90°$.
2. Inclination of the hairs, by reducing the free space between them, results in more efficient protection provided $\theta > 90°$.
3. A system of purely horizontal hairs may in theory give water protection as long as $\theta > 0$.
4. In every case, the smaller the dimensions of the free spaces between the hairs, the more efficient the water protection.
5. In all cases Δp is inversely proportional to a characteristic linear dimension of the hair pile; e.g., in eqn. (16), $\Delta p \propto \frac{r}{(l^2 - \pi r^2)}$.
6. If irregularities exist in the dimensions l and r of the hair pile, only the minimum pressure calculated from the maximum values of l and r can be attained without invasion of the plastron by water.

Biological Efficiency of the Plastron

From No. 4 above, the hairs should, ideally, be as small and as closely packed as possible for the most efficient water protection. But for respiration needs the very opposite condition with the greatest possible free gas-liquid interface is required. Hence a compromise must be made between efficient convection of water and diffusion of oxygen across the boundary on the one hand, and a reasonable margin of protection from wetting on the other.

No. 5 and 6 show that if the fraction of free water surface is kept constant the water-protecting properties may yet be enhanced by reducing the scale of the system and by keeping it quite regular. It follows therefore that an insect adapted to plastron respiration would be expected to have a pile of exceedingly fine, regularly spaced hairs. There is, however, a lower limit to the dimensions of this hair pile quite apart from molecular dimensions. For an efficient distribution of partial pressure over the plastron, it was noted that D and h must be sufficiently large ; hence h (the height of the gas-water interface from the surface of the insect) cannot be reduced indefinitely without an adverse effect on respiration (Fig. 2). Now the resistance to pressure of the bending moment of n hairs per unit area is proportional to $nr^4/h^2 = r^4/l^2h^2$, so that, provided all the dimensions of the system were proportionately increased or reduced, the strength is not altered. If h is kept constant and r and l reduced, a point will be reached when the hairs begin to bend and the plastron to collapse.

This has in fact been observed in *Aphelocheirus*.[7] If placed in clean water to which the hairs present a high contact angle and subjected to 2–3 atm. external pressure, the silvery-grey sheen characteristic of the hair pile and its film of gas suddenly flashes darker, but is restored again when the pressure is reduced. This is quite different from the effect of a wetting agent, when the sheen gives place to a dull black, and moreover the change is then not reversible in clean water and the respiration of the insect is considerably impaired. From dimensions of the hairs and their spacing it was deduced that if the Young's modulus of the hair were in the order of $0{\cdot}5 \times 10^{11}$, bending should occur at an excess pressure of 2–3 atm.

These considerations affect the limits of magnitude of the hair pile. From No. 1 and 2 above, simple vertical or inclined hairs are the least efficient type of structure, the plastron being waterlogged if θ falls below 90°, a somewhat hazardous position. No. 3 shows that horizontally arranged hairs are the best possible form, though in practice their efficiency is less than might be expected from eqn. (18) and (19). This is due to the necessity of keeping the horizontal portions supported in some way, as for instance by having vertical stems bent over at the tip. The bent region adjoining a vertical stem is a point of weakness down which the meniscus tends to travel if θ is less than 90°. The general effect is to cause the menisci to become confluent and to flood out the plastron when β is considerably less than 90°; for instance, if β cannot exceed 30° without instability resulting, the critical contact angle is about 60°, not zero, for spontaneous wetting. This is about the angle found in nature (see Fig. 5). Nevertheless, it offers a much greater margin of safety. When β is small, as for high values of θ, the effect of the vertical portions of the hairs is negligible.

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[7] Thorpe and Crisp, *J. Expt. Biol.*, 1947, **24**, 227.

Another important feature of the plastron is that any breakdown in water protection should be localised. This is generally the case unless the contact angle is greatly reduced by a wetting agent; the upright or inclined portions of the hairs present to the laterally invading water a system essentially similar to that treated above.

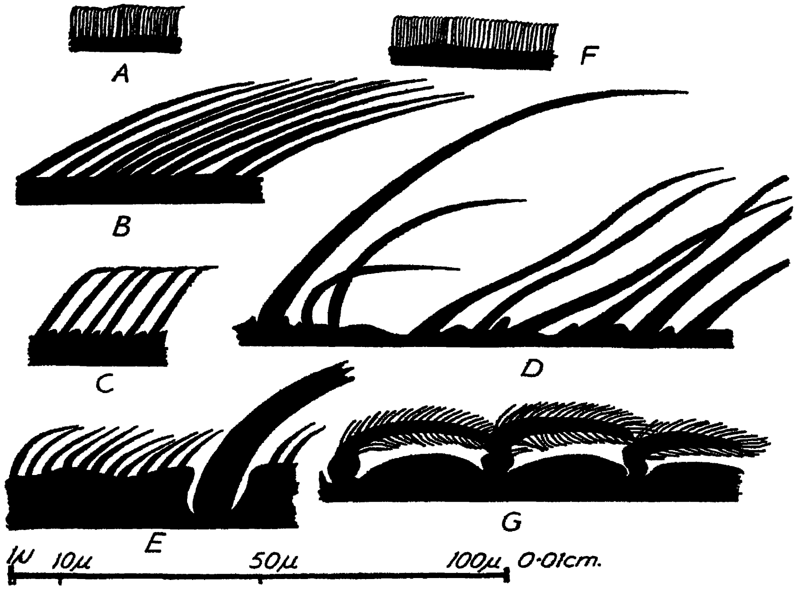

FIG. 4.—Sectional views of hair piles of several aquatic insects drawn to the same scale.
- A. *Aphelocheirus æstivalis* (from abdominal sternum).
- B. *Aphelocheirus æstivalis* (pressure sense organ).
- C. *Hæmonia mutica* (from thoracic sternum).
- D. *Donacia simplex* (from abdominal sternum).
- E. *Elmis maugei* (from thoracic sternum, showing base of one of the macroplastron hairs).
- F. *Stenelmis crenata* (from metathoracic sternum).
- G. *Phytobius velatus* (from abdominal sternum).

The Plastron in Nature

Aphelocheirus æstivalis, a bottom-living bug found in streams and to depths of 7 m. in rivers of Eastern Europe, exhibits the plastron in its most perfectly developed form. The plastron hairs are minute, the dimensions being $r = 1 \times 10^{-5}$, $l = 5 \times 10^{-5}$ cm.; they are neatly and regularly arranged with their tips bent sharply at 90° to present a horizontal "pile" at the interface (Fig. 4 A). The plastron space communicates through radiating channels with open spiracles ("rosettes") arranged in a row down each side of the abdomen. A screen of cuticular filaments beset with fine hairs protects the entrance of each spiracle from ingress of water.

It is obviously impossible to measure the contact angle of these fine hairs against water; we therefore resorted to an indirect approach to study their properties. A series of solutions of butyl alcohol were made up and the contact angle formed by each against a freshly prepared paraffin surface was measured, also the surface tension of each solution. Using the values of θ and γ so obtained the curves in Fig. 5 were constructed by means of eqn. (16)–(19). The experimental points, indicated with crosses, were found by exposing pieces of cuticle bearing the plastron to graded strengths of butyl alcohol in a pressure chamber and determining at what pressure wetting occurred. It is seen that when the contact angle is greater than 90° the $\Delta p - \theta$ curve agrees with that based on eqn. (18), (19) (curve 4), that is with the assumption that the effective regions of hairs are horizontal, circular in cross-section, and have surface properties like those of paraffin wax.

Aphelocheirus carries on either side of the second abdominal segment a small patch of long and much larger hairs which lie almost horizontally overlapping one another (Fig. 4 B). This region is part of an organ of pressure sense,[4] and not being a respiratory area the free space between the hairs is reduced to a much greater degree than elsewhere. They are on this account, in spite of their larger size, more difficult to wet than any other part of the surface. The importance of regularity of the hair pile is well illustrated by two nearly related beetles, *Donacia simplex* and *Hæmonia mutica* (Fig. 4 D and C). The former, which lives in the neighbourhood of streams, is protected by long irregular hairs ($0{\cdot}3 \times 10^6$ per sq. cm.) from the danger of wetting when accidentally falling into the water. *Hæmonia mutica*, however, is a true plastron insect with beautifully regular hairs ($2{\cdot}5$–10×10^6 per sq. cm.) having bent tips and covering the ventral surface of the body and the antennæ. The latter are apparently used to "tap" the oxygen from near the surface of water or from bubbles.

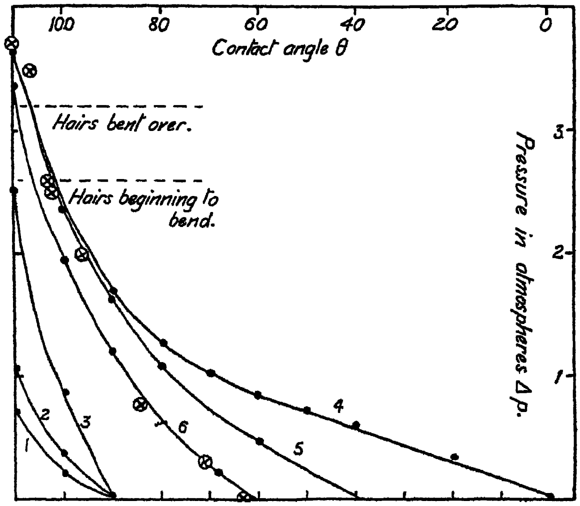

FIG. 5.—Curves to show excess pressure (Δp in atm.) sustained by hair pile of dimensions found in *Aphelocheirus* as a function of the contact angle: 1, vertical hairs (eqn. (16)); 2, hairs inclined at an angle of 45° to horizon (eqn. (17)); 3, hairs inclined at an angle of 30° to horizon (eqn. (17)); 4, horizontal hairs; limiting value of angle $\beta = 90°$ (eqn. (18) and (19)); 5, horizontal hairs; limiting value of angle $\beta = 50°$ (eqn. (18) and (19)); 6, horizontal hairs; limiting value of angle $\beta = 30°$ (eqn. (18) and (19)). Experimental data ⊕.

The *Elmid* beetles possess plastron hairs of similar dimensions to those of *Hæmonia*, but they are less regular and more easily wetted (even gas-free water may be sufficient (Fig. 4 E). However, the plastron here is only a second line of defence; for although it is partially lost by simple diffusion as shown above (since the hairs bend easily under pressure and tend to clump together leaving bare patches), under natural conditions it is actively maintained by the capture of bubbles, for which purpose the limbs are provided with small plastron areas. These same areas are constantly brushed against the main plastron of the body, presumably because it is important to keep the hairs regular by grooming. *Stenelmis crenata* (Fig. 4 F) has a plastron which is very similar to that of *Aphelocheirus.*

In *Phytobius velatus*, a small aquatic weevil, the plastron consists of large, slightly overlapping scales each covered with a fine hair pile. It affords extremely efficient protection against water, comparable with that of *Aphelocheirus* (Fig 4 G).

The Properties and Development of Plastron Hairs

There does not appear to be any evidence that the hairs are rendered hydrophobic by a waxy or oily secretion, as their surface properties are unimpaired and sometimes are actually enhanced after wetting with organic solvents. The hydrophobic properties seem to be due to the nature of the surface of the epicuticle of which the hairs are composed ; the cuticles of certain plants have similar properties [8]

When newly emerged from the last larval instar, the whole animal is always very hydrophobic, but after continual immersion for some months in water, the contact angle of the outer surface becomes as small as 10° or 20°. This effect is confined to the outer side only, there being little evidence that the plastron itself becomes less efficient with age except in the *Elmidæ*, which are rather easily wetted and in other ways exceptional. If the plastron is wetted under pressure or by a wetting agent, the change is irreversible even in water supersaturated with gas, owing to the well-known hysteresis of contact angle [9, 10] In both these phenomena, the contact angle is reduced by contact with liquid water but not by contact with the saturated vapour.

A somewhat puzzling feature is the formation of the plastron under water, in what must be a saturated humidity. The adult cuticle, including the plastron and its gas content, is formed beneath the larval cuticle. In an early stage of development its outer surface is smooth, but shows close-packed striæ perpendicular to the direction of the surface ; later, by resorption of intermediate material, these striæ come to project from the surface into the moulting fluid ; they are the definitive plastron hairs. As late as two or three days prior to splitting off the larval skin, the moulting fluid gives place to a gas layer within the plastron This gas is not derived directly from the air spaces of the insect as there is as yet no connection between them and the plastron ; moreover, active pumping in of gas would not expel the moulting fluid from the minute interstices of the plastron hairs. This must therefore be accomplished by the formation of gas *in situ.*

If it is assumed that gas is actively secreted from supersaturated solution, the pressure must be enough to overcome the surface forces between the moulting fluid and the plastron, and may be estimated from eqn. (18) and (19), employing the minimum value for Δp with the relevant values for β between 0 and $-90°$. Thus taking reasonable values $\theta = 0$, $\gamma = 30$, Δp is of the order of 4–5 atm. The production of so high a pressure is difficult to envisage and, moreover, the plastron after expulsion of fluid would still be wettable if not rendered hydrophobic On the other hand, if by a mechanism of secretion or adsorption, such as would not be hard to envisage, the plastron were rendered hydrophobic, with an equilibrium receding contact angle approaching 90°, the pressure required to force out the moulting fluid would be very much less. The newly exposed surface would be hydrophobic with an advancing contact angle probably $> 90°$, as is indeed found as soon as the plastron is uncovered. If a receding contact angle to water of $> 90°$ were actually achieved, the withdrawal of moulting fluid would be spontaneous, but such a change has never been produced *in vitro.* It is not beyond the bounds of possibility that the living organism may succeed in doing this.

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[8] Fogg, *Proc. Roy. Soc. B*, 1947, **134**, 503.

[9] Bartell and Bristol, *J. Physic. Chem.* 1940, **44**, 56.

[10] Fowkes and Harkins, *J. Amer. Chem. Soc.*, 1940, **62**, 3374.

Summary

Certain insects are adapted to living continuously below the surface of water by retaining a thin film of air next to the body surface as a physical gill. It is demonstrated that this film of air requires to be at a lower pressure than its surroundings, and hence there exists a tendency for the surrounding water to invade it. This is prevented by a pile of small hydrofuge hairs which are frequently capable of holding up the air-water interface against a pressure of several atmospheres Such a gill is termed a " plastron." The diffusion processes within the plastron, and the necessary free water surface for respiration impose certain restrictions on its structure which are not entirely compatible with its water-protecting properties. The solution which offers the best compromise to all the biological requirements appears to be a system of hairs as fine as is compatible with their mechanical strength, with their tips bent over to present a horizontal array to the water surface.

Several types of plastron-bearing insects which illustrate these principles are briefly described. The plastron hairs do not rely on a waxy secretion for their hydrofuge properties. If the plastron is wetted it can only become functional again by drying out; its water-protecting properties are then unimpaired.

The development of the plastron takes place beneath the moulting fluid in a saturated atmosphere; this raises a number of interesting physico-chemical problems and suggests waterproofing occurs beneath an aqueous layer, which is thus more readily withdrawn from the surface, leaving it hydrophobic.

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GENERAL DISCUSSION

Dr. J. W. L. Beament (*Cambridge*) said: It is apparently implied in the introductory paper that Dr. Wigglesworth and I have correlated wax *melting* points with the temperature at which there is a sudden increase in the transpiration through the cuticle of an insect. However, our work shows that the temperature at which transpiration increases suddenly, is consistently a few degrees below the orthodox " melting point " of the extracted wax. We have held that this " transition temperature " corresponds to optical changes in the appearance of the wax: to the temperature at which the wax will spread on water, and will reorientate against a water interface, as shown by measurement of contact angles. These phenomena may correspond to a two-dimensional melting point and appear to fit in admirably with the theories of Dervician which Dr. Schulman has quoted.

Dr. V. B. Wigglesworth (*Cambridge*) said: Dr. Schulman has stated that "there is no evidence that a lipoid monolayer adsorbed onto a solid structure can prevent water evaporation." However that may be, I should like to point out that the wax film on the insect cuticle is in fact laid down upon a moist layer.

Most of my remarks will concern Dr. Hurst's paper. In my opinion the speculations of Dr. Hurst about the nature of the water-proofing mechanism in the cuticle of the blow-fly larva go much further than is justified by the experimental evidence at present available. There are, however, certain points that I should like to raise for discussion.

(i) It is very difficult to obtain evidence for the existence of the different layers of the epicuticle unless the deposition of the cuticle is followed stage by stage. That has not yet been done with the cuticle of the blow-fly larva, but there is some slight evidence to suggest that this may be a somewhat anomalous type of cuticle.

(ii) As to the hardening of the " cuticulin " layer of the epicuticle, I agree with Dr. Hurst that there is an increased resistance to solvents such as nitric acid *before* any tanning occurs. I have suggested that this might result from denaturation of the protein or from polymerisation of the lipides or both. But I have also supposed that subsequently the material is tanned. I note that Dr. Hurst regards the union of lipides with protein and the tanning of protein as mutually exclusive —on the grounds that both lipides and quinones compete for the amino groups.

I should like to ask whether the nature of the link between lipides and proteins is in fact known ?

(iii) Fraenkel and Rudall, who are quoted by Dr. Hurst, showed that there is a lamellar fine structure in the endocuticle. So far as I know a lamellar structure of these molecular dimensions has never been demonstrated in the epicuticle. The sandwich arrangement of lipoids and proteins which Dr. Hurst proposes is a fashionable idea. It may well apply at the insect epicuticle. But if so, it should be possible to get evidence of this by X-ray analysis or other means. No such evidence exists at present.

(iv) Dr. Hurst remarks that "the epicuticle is spatially separated from the liquid water phase by the endocuticle." I do not think that is true Liquid water certainly exists throughout the endocuticle. I believe that in many insects it extends into the substance of the epicuticle right up to the wax layer. I have referred to some of the evidence for this in my paper.

(v) Lastly, there is the question of abrasion of the cuticle by alumina. Alumina is a highly hygroscopic substance. I have never attempted abrasion with it when moist ; but its properties are then so changed that I should not be surprised if it failed to work. I am well aware that the term "abrasion" begs a number of physical questions. I am told that physicists do not know what abrasion is ; until we know more about the physical nature of abrasion we cannot understand the true mechanism of the action of inert dusts on insects. As I pointed out in my original paper on the subject, it may be that the attractive forces at the surface of crystalline particles, which were suggested by Alexander, Kitchener and Briscoe as important in the working of inert dusts, may play a part in abrasive action.

Dr. H. Hurst (*Cambridge*) (*communicated*) : Additional evidence in support of the structure I have postulated in the present paper is given by the diffraction patterns which are produced by transmission through the thin puparial membranes of *Calliphora.* These patterns persist when the cuticle is treated with chloroform, showing that they are not necessarily due to a superficial layer of wax. But they disappear after treatment in strong caustic potash, which is known to break down the structure of the epicuticle. The pattern suggested for a lipo-protein in the appendix to my paper permits the presence of superimposed unit cells of orientated lipid between the protein layers, the fundamental attachments between the lipids and the proteins taking place either by polar association or by non-polar association of the hydrocarbon chains with the non-polar side chains of the protein. It is possible that this latter type of association is involved in the relationship between the mobile waxes and the bound lipoprotein fabric of the cuticle. I hope to obtain further information as to the laminar distribution of lipids and proteins by low-angle incidence X-ray diffraction examination.

Dr. J. W. L. Beament (*Cambridge*) said : I would like to deal with the subject of asymmetry in a little detail as it is one on which I have done some experimental work. Dr. Hurst and I have both recorded that insect cuticle transmits water more rapidly in the direction epicuticle → endocuticle, than when reversed, when it is the barrier between liquid water and unsaturated air.

Dr. Hurst has proposed a hypothetical structure to explain the asymmetry of *Calliphora,* in which the epicuticle acts as a "valve." It does not seem to me that such a complicated structure is at all necessary. Dr. Hurst states "a layer of wax beneath the endocuticle should restrict the passage of water in the same way as a layer on the surface," and later, "a superficial wax layer would restrict the passive flow of water," (thus agreeing with the general theory), "but is inconsistent with selective directional flow." I would hold that it is essentially a layer of wax which causes asymmetry.

My own experiments indicate that the cuticles of a number of insects are asymmetric in that they transport water more rapidly into dry air in the direction epicuticle → endocuticle, than when reversed. This holds for the intact cuticle of three very different insects and two ticks, for the cast skin of two insects and a tick, for a number of waxed lipoid-free skins and cuticles, for waxed tanned gelatin and waxed porous pot. None of these membranes, when wax free show any detectable asymmetry. An insect wing consists of lipoid-epicuticle-endocuticle-

endocuticle-epicuticle-lipoid and it is most important to stress that it is theoretically and practically symmetrical, whether intact or after extraction with chloroform. But when waxed on one side such a membrane is asymmetric.

I do not claim that the figures involved in my experiments show such a large ratio for asymmetry as those of Dr. Hurst. The greatest asymmetry I have detected is fivefold, and I feel that this reading is large. For it must be understood that insect cuticle is very easily damaged and an experiment must be carried out very carefully to ensure that, on reversal, a membrane is structurally unchanged. In most of my experiments the membrane has been cemented between two celluloid rings held between rubber gaskets. The whole ring is removed for reversal. Even so, the operation of removing the preparation in its celluloid holder and replacing it *in the same direction*, may double the recorded permeability. An apparatus has also been used in which water could be placed on either side without disturbing the membrane at all.

I would be grateful for the guidance of physical chemists on these ideas, but it would seem to me that a waxed membrane can give rise to one of two kinds of asymmetry. It is, for instance, well known that a piece of paper, waxed on one side, is asymmetric when tested under the conditions which we have mentioned. This fact has been used in the packing of commercial articles. Its asymmetry is, however, reversed with respect to insect cuticle, i.e. water passes more rapidly in the direction water-paper-wax-air, than water-wax-paper-air. The explanation is straightforward. We assume the wax has the same permeability in both cases. In one, the paper is wet and permeable, in the other it is in dry air receiving very little water and the dry material has a much greater resistance to the passage of water. Asymmetry will be shown by any membrane where the non-waxy lamina changes its permeability to water with its degree of saturation.

The insect cuticle is not unique in having the other kind of asymmetry; it has been reported by Denny (1917) for the wax-covered coats of seeds, and by Hamburger (1926) for synthetic systems. Now we do *not* postulate that the wax layer on the insect or membrane is *impermeable* to water; we say that it is resistant to the passage of water through the intermolecular spaces in the wax layer. In all the membranes in which this kind of asymmetry has been shown, the non-waxy side is porous and remains rigid and porous when desiccated. If water is to pass through the wax more rapidly in one direction than in the other, we must assume that the forces acting on that water are, when summed, greater in the one case than in the other.

When the waxed surface is against air, the force pulling out the water is that of the saturation deficiency of the air. The hydrophilic lamina of the membrane is unsaturated, with a gradient through its thickness (otherwise water would not flow through it) and as it is unsaturated, this will tend to restrain water from passing into the wax. As water does not spread readily over a hydrophobic substance, such as we imagine will line the waxy pores, evaporation must take place from the bottom of these pores, and is very restricted. When the membrane is reversed, the wax is in contact with liquid water, which can be regarded at zero potential, and there is no retarding effect. On the other side a comparatively dry, porous, hydrophilic lamina is capable of absorbing water at a great rate. Water will spread along the pores of this material rapidly, so that it reaches the surface quickly and presents a large area for evaporation at the *upper* surface. It would seem possible that there is a continuous liquid water phase through the wax under these circumstances, where every pore for evaporation from the wax is now a channel for water entry. If the wax is porous on a more macroscopic scale, this theory will work equally well.

The wax layer itself has not been looked upon as a totally symmetrical layer. One side has been assumed to be closely packed and orientated; but "the additional effect of the remainder of the wax depends on its close packing" (Beament, 1945) and, especially as the molecules are not uniform in length, the arrangement must become more and more irregular towards the upper surface of the layer. I understand that a tightly packed monolayer presenting a surface of molecular endings will not be easily penetrated by water. This structure will be operating in the "normal" cuticular condition. On reversing the membrane, the unorganised molecules are in contact with water, and more readily wetted and penetrated. This effect must add to the degree of asymmetry which is measured.

Dr. G. S. Hartley (*Harston*) said: With regard to the paper of Hurst, he thought that it had not been shown to be necessary to invent highly specialised mechanisms for producing asymmetrical diffusion through membranes. He wished to bring two known factors together to predict with confidence that, in any membrane having a difference of permanent composition, chemical or structural, between its several layers, different rates of penetration in the forward and backward directions were to be quite generally expected.

The first fact was that in any membrane, initially homogeneous but considerably swollen by the penetrating substance, the diffusion coefficient depended greatly on the concentration of the latter, being higher the higher this concentration. As a result, at any one steady state, a gradation of diffusion coefficient across the membrane existed. On reversing the membrane, the gradient would be reversed and no asymmetry would be found.

The second fact was that in any intrinsically (permanently) composite membrane, the diffusion coefficient would vary from one side to the other, even if the swelling were so small that the penetrant substance did not itself change the diffusion coefficient in any one part of the membrane. In this latter case it could be shown that here, too, no asymmetry of penetration rate would occur.

When, however, these two factors combine, the diffusion coefficient being a function both of the dry composition of the membrane and of its degree of swelling by the penetrant substance, the diffusion coefficient-distance function across the membrane could be qualitatively and quantitatively different for the two positions and asymmetry of penetration could quite generally result.

Put briefly as a mathematical statement, we can easily show that if x is distance through a membrane and c is concentration, having uptake and exit values at O and X of c_2 and c_1, the rate of transfer per unit cross-section G is given by

$$G = -D\frac{\mathrm{d}c}{\mathrm{d}x} = -\mathrm{f}\,(x, c)\frac{\mathrm{d}c}{\mathrm{d}x}$$

in the general case. If the complex function $\mathrm{f}\,(x,c)$ is expressible as the product of two unique functions $\mathrm{f}_x(x) \times \mathrm{f}_c(c)$, this becomes

$$G\int_{0}^{X}\frac{\mathrm{d}x}{\mathrm{f}_x(x)} = \int_{c_2}^{c_1}\mathrm{f}_c(c)\mathrm{d}c.$$

In this case, since

$$\int_{0}^{X}\frac{\mathrm{d}x}{\mathrm{f}_x(x)} = \int_{X}^{0}\frac{\mathrm{d}x}{\mathrm{f}_x(X-x)}$$

the permeability of the membrane will be symmetrical. Such separability of $\mathrm{f}\,(x,c)$ into the product of two unique functions will not, however, be realised in practice except in the more limited case of one of them being constant, i.e. the membrane will only be symmetrically permeable if D is constant or a function of x alone or c alone. Where D is a function of both x and c it is extremely improbable that the function will be separable and, if not, asymmetric permeability is to be expected.

Dr. W. W. Barkas (*Princes Risborough*) (*communicated*): As a supplement to Dr. Hartley's useful remarks on asymmetrical diffusion in homogeneous membranes, may I point out that there is no reason for supposing that diffusion should normally be expected to be more rapid when the more permeable material faces the higher vapour pressure, though this is true I believe of many coated papers? If the increasing permeability with moisture content of the more permeable layer is due to swelling, as Hartley, I think correctly, suggests, then if the same layer is not allowed to swell freely, it may well be less permeable when wet than dry. If, therefore, the less permeable layer in the membrane prevents the free swelling of the other, the greater net permeability of the composite membrane may be found when the less permeable layer faces the higher vapour pressure. Hartley's analysis is correct if, as I am sure he intends, that the permeability of the separate layers are those obtaining in the membrane itself, and not those measured on layers which have been separated from the membrane.

Dr. A. Klinkenberg (*The Hague*) said: According to Dr. Schulman the wax layer of the cuticula will be impermeable to water only where it is well orientated. For this, it is necessary that it rests on a wet surface, i.e. the polyphenol layer. It seems to me that wetting the wax layer on the outer surface also removes the cause for orientation. The layer might therefore disorientate in the experiments on the inward penetration of water through insect cuticula and become permeable to water.

Dr. Hartley has put forward the argument that an asymmetrically built-up layer, in which the diffusion coefficient for water depends on the equilibrium partial pressure, will show unequal rates of transport of water in both directions. It is possible to differentiate between these two causes of asymmetry of the movement of the water. The first should disappear when experiments are made with water vapour of different pressure on both sides of the cuticula, instead of using liquid water on one side and vapour on the other.

Dr. H. Hurst (*Cambridge*) said: It has long been known that membranes may be more permeable in one direction than in the reverse direction.[1] [2] I have referred elsewhere to the analogy between the permeability of insect cuticle and the waxy cutinised layer of plant membranes, such as the skin of the tomato or grape.[3] Both the insect cuticles and plant membranes are most permeable to water when the outer surface is in contact with the liquid water phase. Moreover, the penetration of ethyl alcohol through the tomato skin is increased in the presence of kerosene, in the same way as the cuticle of *Calliphora* larva is made many times more permeable to alcohol by kerosene or benzene. These effects are reversible, for if the insects are transferred from the mixed solvent system to pure alcohol, the rate of penetration is slowed down.

The *Calliphora* cuticle is also analogous to a rubber membrane, which is unvulcanised, or partially vulcanised.[3] For example, the permeability of a rubber membrane to ethyl alcohol is increased by a swelling solvent, such as benzene, carbon disulphide, carbon tetrachloride, or kerosene, but not by a non-swelling solvent, such as castor oil. Kerosene may increase the rate of penetration of alcohol through the insect skin several hundred times, but castor oil, or oleic acid does not have this synergistic effect. This combined action of kerosene and ethyl alcohol is shown with the waxy type of cuticle, but only after a moult when the cuticle is soft. Similarly, thin sheets of hard vulcanised rubber do not show the effects of induced penetration of alcohol by a swelling solvent.

These effects, of course, do not prove that the structure of insect cuticle is similar to that of a plant skin; or rubber membrane, but they suggest that the permeating medium may greatly increase the permeability of the cuticle by swelling the structural framework, and that this is inhibited by the introduction of chemical cross-linkages into the fabric which restrict the separation of the structural elements.

In his contribution to this Discussion, Dr. Beament distinguishes between the waterproofing action of a wax layer system and of a protein *impregnated* with wax. He points out that the properties of a wax-protein system, as revealed by the actions of poisons, detergents, and abrasives, are altogether different from those of a lamina of wax, which is said to be the normal water-proofing mechanism in insects. In particular, the wax laminæ show sudden increases in permeability to water at critical temperatures, while this property is not shown by the wax-protein system in the *Rhodnius* egg-shell. Let us examine further this conclusion in the light of experimental evidence.

In Fig. 2 of his contribution to this Discussion, Dr. Wigglesworth shows that in different species of insects with waxy cuticles, there is a sudden increase in permeability to water at temperatures within the range 30° c. to about 60° c. The respective critical temperatures correspond closely with those obtained with isolated layers of wax deposited on insect wing membranes. From the quantity of wax, obtained by treating the isolated cuticles with boiling chloroform, Dr. Beament has calculated that the waterproofing layer consists of a layer of wax 0·2–0·3μ thick on the surface of the tanned protein cuticulin layer.

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[1] Hamburger, *Biochem. Z.*, 1908, **11**, 443.
[2] Denny, *Bot. Gaz.*, 1917, **63**, 373.
[3] Hurst, *Nature*, 1941, **147**, 388.

There is an extraordinary coincidence between the critical temperatures (41° c.) for the feeding larva, prepupa, and early puparium (24 hr.) of *Calliphora.*[4] This coincidence extends to the critical temperature (41·5° c.) for the membrane systems containing isolated wax. At these critical temperatures the insects and the model membranes permit the passage of water at a rate of 5 mg./sq. cm./hr.[5] By weighing the wax extracted from the washed puparia, Dr. Beament has calculated that the thickness of the superficial waxy layer in *Calliphora* puparia, and presumably, in the larval stages, is 0·27μ.

From the physico-chemical point of view, the similarity between the behaviour of the *Calliphora* cuticle and the waxed membrane provides critical evidence that there is a superficial layer of wax on the surface of the insect cuticle, and this layer of wax is the main barrier to water loss from the cuticle.

From the biological point of view an unfortunate snag arises. There is no superficial waxy layer on the surface of the cuticle of *Calliphora* larvæ. During pupation, the larval cuticle is transformed into the hardened puparium, which becomes a dead structure, in which there can be no secretion of a waxy layer. Dennell has similarly reported the absence of a superficial waxy layer in the related blowfly larva, *Sarcophaga falculata.* Dennell[6] has pointed out that in the cuticle of *Sarcophaga,* it is the outer layer of the epicuticle which is *impregnated* with lipid, in the sense implied by Dr. Beament. In fact, the chain of evidence clearly shows that there is a similarity between the behaviour of the wax-protein protective layer and a lamina of wax. The technique used by Dr. Beament for removing the waxes from insect cuticle does not differentiate between a superficial layer of wax and wax present in the underlying cuticulin layer, although a proportion of this wax may be strongly linked to the structural protein. The wax-protein in the *Rhodnius* egg-shell must either possess peculiar properties, or its permeability is influenced by other factors.

A model membrane consisting of a homogeneous layer of wax on a permeable supporting framework merely indicates that the lipids of the cuticle have water-proofing properties either in a superficial layer or when associated with protein in the epicuticle framework. It is by the appropriate selection of biological material that the model system is shown to be inadequate from a biological point of view, for Dr. Beament has described and measured the thickness and permeability of a superficial wax layer on the surface of the cuticle of *Calliphora* when no such wax layer exists. If we consider the physiological significance of cuticle structure in relation to the flow of water through the membrane, it is possible to select quite a number of simple membrane systems which are selectively permeable to water in one particular direction, and impermeable in the reverse direction. By discarding systems which do not conform to the physiological and toxicological requirements of the living systems it becomes possible to arrive at a structure which is fundamentally a laminated lipo-protein in which more labile lipids can participate.

SYSTEM 1.—Double membrane consisting of homogeneous lamina of wax on surface of permeable supporting framework (Fig. 1 (*a*), (*b*)). By definition, the wax lamina is completely impermeable to water. The permeability constant of the double membrane is determined by the permeability constant of the wax lamina, which is zero. The double membrane will not show a directional effect in relation to the evaporation of water through the membrane in opposite directions, and is thus not analogous to insect cuticles of the waxy, or non-waxy type.

SYSTEM 2.—As in System 1, but the waxy layer is penetrated by a series of pores (Fig. 2 (*a*), (*b*)). If the hydrostatic pressure of the water phase in (*a*) is sufficient to force the water into the openings of the capillaries, the rate of evaporation of water is proportional to the area of exposed liquid water $(s_1 + s_2 + s_3 + \ldots s_x)$. In the reversed system (*b*), water will flow from the capillaries into the permeable membrane component, and the rate of evaporation is proportional to the free water surface S, which depends on the true geometrical surface of the membrane. The coefficient of asymmetry is given by the ratio $S(s_1 + s_2 + s_3 + \ldots s_x)$. With systems of this type consisting of a layer of beeswax or paraffin wax melted on to the surface of parchment, I have obtained coefficients of asymmetry of 20–60. The wax layer is perforated by a single pore, 0·2 mm. diam. The membrane is attached to the osmometer described in the present paper, and the hydrostatic pressure adjusted so that the surface of the water in the pore is approximately level with the surface of the surrounding wax layer.

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[4] Wigglesworth, *J. Expt. Biol.*, 1945, **21**, 97.

[5] Beament, *J. Expt. Biol.*, 1945, **21**, 115.

[6] Dennell, *Proc. Roy. Soc. B*, 1946, **133**, 348.

Membranes of this type are relatively impermeable to water in the direction parchment→wax, and permeable to water in the reverse direction. They therefore simulate the two fundamental properties of insect cuticle which have been described. The analogy breaks down on physiological and toxicological grounds. If pores are present in the protective epicuticle layer and these pores are filled with water which does not spread over the general cuticle surface, contact of the cuticle with a hydrophilic surface should induce a bulk flow of water through the pores on to the surface. This does not occur, and it has been pointed out that the surface of the cuticle in blow-fly larvæ is strongly hydrophilic and readily wetted by water. Moreover, lower primary alcohols, such as methyl or ethyl alcohol, do not penetrate through the protective layer. As the homologous series of alcohols is ascended, the molecular volume increases uniformly, but penetration reaches a maximum at amyl alcohol and then falls off. This shows that the protective layer does not act as a simple molecular sieve, and that other factors are involved in alcohol access.

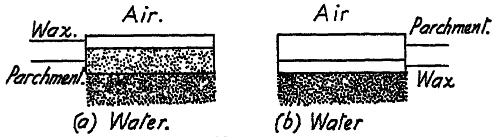

FIG. 1.

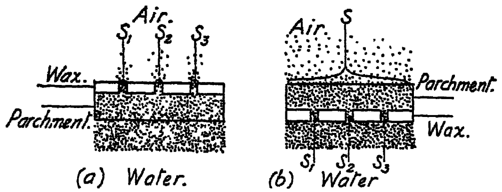

FIG. 2.

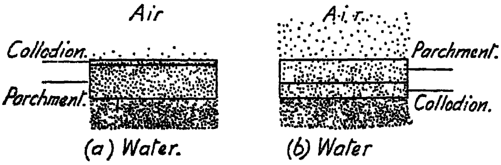

FIG. 3.

In the above systems, the rates of evaporation of water are greater in 2(*b*), 3(*b*) than in 2(*a*), 3(*a*). This directional effect is not shown in 1 (*a*), (*b*). Asymmetrical behaviour in Fig. 2 depends on the difference in wetting properties of the outer surface. In Fig. 3, the swelling of the flexible collodion membrane is the limiting factor.

SYSTEM 3.—Double membrane consisting of a layer of collodion on surface of parchment layer (Fig. 3 (*a*), (*b*)). I have referred elsewhere to the asymmetrical behaviour of collodion-parchment membranes, the system being more permeable in the direction collodion→parchment than in the reverse direction.[2] This may be due partly to the difference in the wetting properties and geometrical surface of the components, as in System 2, but another factor must be taken into consideration. Collodion membranes are usually prepared by allowing a thin layer of collodion solution in an organic solvent (mixture of alcohol and ether) to dry. If water is added before the solvents have evaporated, a "wet" membrane is obtained with large pores. If the membrane is allowed to dry before adding water, a " dry " or " tight " membrane is obtained with small pores. The " wet " membrane is considerably more permeable than the " dry " membrane. The permeability is dependent on the spaces between the micro-crystals of nitrocellulose, and also on the intermolecular spaces between the component molecules of the crystals Northrop [7] has pointed out that in the " dry " type of membrane, the pores are extremely small or absent so that permeability depends on solubility in the membrane.

A collodion membrane is insoluble in water but swells so that there is an increase in the effective free pore space within the membrane. The permeability constant of the membrane to water is therefore a function of the change in permeability induced by the presence of water in the membrane. The general condition for selective directional flow of water through a double membrane system consisting of two components A, and B, is that the permeability constant of one component should increase more rapidly with uptake of water than the other component. Using " tight " collodion membranes deposited on writing parchment, I have obtained coefficients of asymmetry of 4–8, the rate of evaporation of water being greatest in the direction collodion→parchment. This would suggest that the collodion layer is analogous to the epicuticle, and the parchment to the endocuticle layer of insect cuticle.

The influence of the solubility of a permeating medium on membrane permeability can readily be demonstrated with collodion parchment systems, using the osmometer technique described. In the systems

(*a*) water | parchment | collodion | ethyl alcohol vapour (saturated)

(*b*) water | collodion | parchment | ethyl alcohol vapour (saturated)

the alcohol vapour in (*a*) is rapidly imbibed by the exposed collodion layer, and liquid alcohol diffuses into the bulk water phase. The rate of uptake of alcohol vapour is greater than the rate of evaporation of water in the reverse direction, so that there is an increase in volume of the aqueous phase. In (*b*), the increase in the permeability constant of the collodion membrane by alcohol is smaller, and the rate of evaporation of water is the limiting factor which results in a decrease in volume of the aqueous phase.

Certain insect cuticles resemble collodion membranes in the above systems. For example, larvæ of *Chironomus*, which live in water, swell rapidly when placed in ethyl alcohol. If the insect is turned inside out, the tissues removed, the cuticle shell filled with water and the ends ligatured, the " insect " shrinks when immersed in alcohol. Selective permeability to alcohol clearly depends on contact of alcohol with the epicuticle. Similar results are obtained with blow-fly larvæ, but only after treatment in hot fat solvents which remove the labile lipids. The selective effect is influenced by the properties of the bound lipo-protein of the epicuticle framework. Even after *Calliphora* larvæ have been treated with boiling chloroform, the rate of penetration of alcohol through the cuticle is increased by a non-polar solvent, such as benzene, or kerosene. This can only be ascribed to a swelling action of the fat solvent on the bound lipo-protein of the epicuticle, because the permeability of a lipid-free protein membrane such as tanned gelatin is not increased by a fat solvent in this way. It would appear that the cuticulin layer of the epicuticle is not directly analogous to a tanned protein membrane as postulated by Dr. Wigglesworth and by Dr. Beament. The selective permeability of the epicuticle is dependent on the labile lipids and on the bound lipo-protein. The unit of molecular organisation would appear to be a flexible lipo-protein, the variable component being the fat-soluble lipid which is displaced from this lipo-protein.

LIPO-PROTEIN STRUCTURE OF EPICUTICLE.—Experiments on isolated cuticles have shown, that water and non-polar fat solvents, such as benzene or heptane, evaporate most rapidly through the cuticle in the direction epicuticle→ endocuticle. This directional effect is not shown when the outer epicuticle layer is removed mechanically from the underlying endocuticle. The selective effect, however, is shown after the fat-soluble lipids have been removed in boiling chloroform. The permeability constant of the epicuticle to water and fat solvent increases with uptake of these media more rapidly than the permeability constant of the endocuticle, which is analogous to a porous parchment membrane.

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[7] Northrop, *J. Gen. Physiol.*, 1929, **12**, 435.

The analogies between the various layers of the insect cuticle and artificial membranes can be summarised as in Table I.

TABLE I.—ANALOGIES BETWEEN COMPONENT LAYERS OF INSECT CUTICLE AND ARTIFICIAL MEMBRANE SYSTEMS.

Insect cuticle layers.	Composition.	Artificial membranes.
Superficial wax layer.	Long chain fatty acids and alcohols.	Extracted wax film on supporting fabric.
Cuticulin layer.	Flexible lipo-protein * with labile lipid.	Collodion rubber.
Exocuticle.	Tanned protein associated with chitin.	Tanned gelatin.
Endocuticle.	As above (untanned).	Gelatin parchment.

* This becomes quinone-tanned during hardening.

Dr. Wigglesworth and Dr. Beament have based their concept of cuticle structure almost entirely on a model system of a layer of wax, which certainly may be a limiting factor in relation to the passive flow of water through the cuticle in the direction endocuticle → epicuticle. The condition for directional permeability is that the non-flexible lamina of wax should be penetrated by fine pores, a condition which does not exist in the living insect. Any demonstration of asymmetrical behaviour with the model system may simply indicate that small holes interrupt the continuity of the wax layer. If, however, a superficial layer of wax, not necessarily homogeneous, is associated with the underlying flexible lipo-protein framework of the cuticulin layer, so that the wax may extend or "impregnate" this layer, a pattern is obtained which is consistent with histological evidence for the structure of cuticles of the waxy and non-waxy types.

LAMELLAR ORGANISATION OF LIPIDS IN EPICUTICLE.—With the usual staining techniques I have been unable to detect laminations in the epicuticle layer, a point which has been raised by Dr. Wigglesworth. I have inferred the existence of a lamellar fabric from the selective access of catechol through the cut surface of the epicuticle, and from physiological grounds that the natural phenol secreted by the epidermal cells becomes selectively localised in the outer layers of the cuticle. In *Calliphora* larva, or *Musca* larva, there is no superficial wax layer, and a selective storage of polyphenol, which does not pass readily across the cuticle framework, can only occur if the protective lipid is discontinuous. This necessitates the secretion of polyphenol directly into the outer layers through specialised ducts, which can readily be demonstrated by treating the outer layers of the cuticle with ammoniacal silver solution or aqueous catechol solution. The reagents penetrate selectively through the thin layers of epicuticle which cover the distal terminations of the ducts. I am pleased that the lamellar structure for the epicuticle, which I have postulated from permeability measurements should correspond closely with that observed by Dr. Thorpe in the epicuticle of *Aphelocheirus* by the use of ultra-violet photomicrography.

I have not produced direct evidence for the molecular organisation of the structural lipo-protein lamellæ.† I hope to have more information on this point from X-ray diffraction studies on isolated epicuticle. I have depicted the lipid molecules as orientated double layers between protein leaflets. This type of structure has been described for the cell membrane, and for the thicker nerve myelin sheath, which appears to be composed of concentrically arranged lipo-protein layers. The X-ray evidence shows that the mobility of the lipids in the layers depends on the hydration of the sheath.

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† Electron diffraction techniques have since directly confirmed the laminar lipo-protein structure.

From the point of view of directional permeability of insect cuticle, the packing between the hydrocarbon chains will undoubtedly influence the passage of water in the same way as the permeability of an orientated monolayer of wax at an air-water interface changes with surface pressure. If we consider the change in the permeability constant with uptake of water, there is no fundamental distinction between the intermolecular "pores" between adjacent hydrocarbon chains in the monolayers of orientated lipid and the pores in a "tight" collodion membrane. That there is an extremely stable linkage between the lipids and structural proteins is shown by the action of fat solvents and fat solvent mixtures. It is therefore by postulating a change in the hydration of the structural proteins that we can explain the magnitude of the change in permeability constant, since any extension of the protein fibrils will be reflected in an analogous separation of the hydrocarbon chains of the lipids. It is for this reason, that a fat solvent such as kerosene, which increases the permeability of the lipids to other fat solvents, such as ethyl alcohol, also increases the permeability of the cuticle to water. Since the endocuticle is poor in waterproofing lipids, there is only a small increase in permeability constant with hydration, and so the essential conditions for directional permeability are fulfilled. This explains the similar directional effects observed with water and with fat solvents.

Action of Phospholipids.—Further evidence that a simple wax layer is not the limiting factor in passive permeability to water is seen from the waterproofing action of the phospholipids, lecithin and cephalin. That these can penetrate through the cuticle framework is shown by the removal of fat-soluble lipids from the outer surface of the cuticle by chloroform, and the substitution of these lipids by the phospholipids which are present inside the insect. Here is an example of a reversible association between the labile lipids and the bound lipo-protein of the epicuticle. The presence of liquid water is essential for the mobility and orientation of the phospholipids within the epicuticle, and here again a lamellar lipo-protein fabric is consistent with the physiological situation.

When lecithin is applied externally to the waxy cuticle of *Tenebrio* larvæ, the rate of evaporation of water through the cuticle is increased and the insect dies from desiccation.[3] Dr. Wigglesworth has confirmed this observation using various species of insects with waxy cuticles.[4] This apparent discrepancy is perhaps the key to the true significance of a superficial protective waxy layer. Kerosene or benzene increases the permeability of the cuticle of *Tenebrio* to ethyl alcohol, only when the cuticle is soft and flexible, after a moult, and this effect is shown with the adult beetle shortly after emergence from the puparium. As the cuticles harden the synergistic action between kerosene and alcohol diminishes and is not shown with the hardened cuticles. It is also not shown with the puparium of *Calliphora* after this has hardened. This hardening extends to the cuticulin layer of the epicuticle and reduces the flexibility and hydration of this layer. Lecithin would therefore exert a detergent action on the superficial waxy layer in the sense used by Dr. Wigglesworth. Since the underlying lipids in the cuticulin layer are immobilised by the tanning of the associated protein components, there would be little tendency for the lecithin to penetrate and become adlineated with these structural lipids. In this respect, therefore, the concept of a superficial layer of wax on a tanned protein cuticulin layer is fundamentally consistent with the flexible lipo-protein non-waxy type of cuticle described in my paper.

Mosaic Structure of Epicuticle.—The histological evidence clearly reveals the presence of an anastomosing fibrous network in the cuticulin framework of the epicuticle, and this is apparently continuous with the distal branched ends of the pore canals in *Sarcophaga* larvæ. This type of fibrillar network is by no means uncommon in natural membranes. It is possible that the structure serves a mechanical function, for the pore canals in the mature larva become blocked internally with chitin, and they are not connected to the epidermal cells at a stage before the secretion of polyphenol takes place.[6] This secretion therefore cannot take place through the pore canals as Dr. Wigglesworth has described for *Rhodnius* cuticle.[8] In the present paper, it has been assumed that the mosaic network exerts a mechanical function in so far as it restricts the extension of the lamellar lipo-protein framework of the epicuticle. But it is possible, and indeed likely, that in the younger larva, and in other insects, the mosaic elements are continuations of the pore canals into the actual cuticulin framework, and transport and maintain an essential balance of lipid and lipoprotein within the framework or in the superficial waxy layer.

Dr. J. W. L. Beament (*Cambridge*) said : The permeability given by Dr. Hurst for *Calliphora* cuticles in the direction water-endocuticle-epicuticle-air, is at least eight times the value given by Dr. Wigglesworth for the intact insect (which has no active waterproofing mechanism) or by myself for a membrane coated with *Calliphora* extracted wax. It might seem that his cuticle preparations start their experiments in a damaged state.

The Salt-Hollick machine for extracting soil larvæ by flotation, fails to remove many Dipterous larvæ, the group of insects of which *Calliphora* is a member. As this machine seems to depend on the wetting properties of the cuticle, it may point to some peculiarity of these cuticles as compared with other insects.

Dr. J. W. L. Beament (*Cambridge*) (*communicated*) : In reply to Dr. Hurst's addenda to the Discussion, the following points are of interest.

It should be clear from my contribution to the Discussion that only the secondary waterproofing system of the *Rhodnius* egg-shell is suggested as a wax-impregnation of protein since its properties are entirely different from the primary waterproofing system which is of the normal and typical wax lamina type.

Dr. Hurst says " From a physico-chemical point of view . . . a wax layer is the main barrier to water loss." If this is admitted, the biological evidence rests with Wigglesworth's work on the deposition of the cuticle in *Rhodnius*. Dr. Dennell has *not* reported the absence of a wax lamina ; he has failed to demonstrate one histologically—which applies equally well to the work of Wigglesworth and others in this field. Surely no conjecture on the structure of the *Calliphora* cuticle is valid until the deposition of its cuticle has been followed ?

Calculations of wax thickness have always been based on the assumption " if this wax is distributed as a uniform layer over the surface of the cuticle."

Dr. Hartley and I have given ample reasoning that a wax lamina system will account for asymmetry without the introduction of more complex structures for which no reliable evidence exists.

Dr. H. Hurst (*Cambridge*) said : Dr. Beament has criticised the experimental data in my paper in three respects.

(1) He states quite positively that he has never been able to obtain asymmetry coefficients greater than 5, and that some experimental error is responsible for the higher coefficients recorded in my paper. This statement is not in accord with his published statement in the original paper on which his communication is based.[6] Referring to the data in Table 1, p. 116, Dr. Beament reaches the following conclusion :

" These results confirm the observation of Hurst[3] (1941) that there is an asymmetry of one hundredfold in the transmission of water through the blow-fly larval cuticle. There is a suggestion of asymmetry in the whole cuticle, but in the exuviæ of *Rhodnius* the ratio of rates of transmission of water in either direction are 20 : 1 in the initial period, and 5 : 1 *after the membrane has been exposed to water for* 21 *days and is very fragile.*"

This conclusion is remarkable, for I have found that the high coefficients of asymmetry are only obtained when the live insect is killed and *quickly* dissected under water. There is a rapid elution of water-soluble proteins and probably lipo-proteins from the cuticle framework. This is reflected in the progressive increase in the rate of evaporation of water in the direction endocuticle→epicuticle. During the first 10–20 min. the rate of water loss is so low that it cannot be measured accurately with the apparatus used, which is adapted to utilise maximum cuticle surface, and can register changes accurately to 0·1 mg.* In Fig. 2, it is seen that the rate of water loss increases considerably (r_1) after about 40 min., and this results in a decrease in the coefficient of asymmetry.

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[8] Wigglesworth, *Proc. Roy. Soc. B*, 1947, **134**, 163.

In the technique used by Dr. Beament, the isolated cuticles are left in distilled water overnight, attached to the membrane holder, and the whole apparatus left in a desiccator for 24 hr. before taking readings. These were obtained by weighing at intervals of 24 hr. This technique is discontinuous and is not suitable for measuring changes in permeability, which take place rapidly in the presence of water. Dr. Beament refers to the coefficient of 5 : 1 in the fragile cast skin of *Rhodnius* which has been exposed to water for 21 days, but gives no indication of the actual rates of evaporation of water in opposite directions through the membrane.

(2) Dr. Beament refers to the fact that the rate of evaporation of water through the isolated cuticle of *Calliphora* is greater than that recorded by Dr. Wigglesworth for the cuticle in the intact insect.

This criticism is answered in my initial comments. The permeability of the cuticle increases owing to the passage of water-soluble or dispersible materials from the endocuticle into the water in the osmometer tube. If lecithin or cephalin are present in the water phase, the rate of evaporation of water is reduced (Table III).

(3) Dr. Beament comments on the high rate of evaporation of water in the direction epicuticle→endocuticle and points out that this is greater than the rate of evaporation from a free water surface.

The free water surface of the endocuticle depends on the true geometrical area, over which the permeating water spreads The rate of evaporation of water from a free water surface may be greatly increased if a thick layer of blotting paper is placed in contact with the surface. In his calculations of the effective thickness of wax layers on the cuticle, Dr. Beament has ignored this factor.

Dr. J. W. L. Beament (*Cambridge*) (*communicated*) : The original report of asymmetry in *Rhodnius* cuticle was a preliminary one. These results have been discarded with the use of more reliable and efficient apparatus. Nevertheless, in contradiction of Dr. Hurst's assertion, the actual rates of evaporation on which these ratios were calculated *were* published in the original paper to which Dr. Hurst refers.

The figures for permeability in the original paper are steady values. It would indeed be difficult to ascribe reasons for the changes in permeability over an initial period, such as an hour or even smaller intervals of time. During this time, the water content of the membrane at the time of setting up, its state of tension under the rubber band (!) and water on its external surface are each factors which would make extrapolation a risky matter.

Minute irregularities in cuticle surface have been taken into account in the calculation of apparent wax thicknesses. This does not affect the issue that the only reasonable test of identity of conditions in a membrane of cuticle and in the intact insect, is, that the rates of evaporation through each should be almost identical.

Dr. A. D. Lees (*Cambridge*) said : It seems questionable whether a cuticle with the structure pictured by Dr. Hurst in Fig. 6 could effectively restrict transpiration. In this model the epicuticle is shown as a mosaic of lipo-protein leaflets enclosed by a "flexible restraining network" of vertical rods. The latter elements are not stated to contain lipids and are presumably thought of as hygroscopic. But since they penetrate to the surface of the cuticle, what is to prevent rapid evaporation occurring at these points ? The same concept has also been applied by Dr. Hurst in interpreting the phenomenon of the active water uptake through the cuticle of living insects. From a general standpoint, however, it would seem unwise to ascribe to the physical properties of the cuticle a dominant part in this function ; for, whereas the structure and properties of a wide range of arthropod cuticles appear to be rather uniform, the ability to secrete water in this manner is certainly rare. Criticism could also be levelled at the implied mechanism of withdrawal of water from the cuticle. It seems dubious whether tensile forces, developed in the body wall as a result of random muscular contractions, could ever be an effective agency in expelling water from the cuticle; and this view, of course, ignores the undoubted role of the epidermis in controlling the passage of water. Finally, there is no evidence that any reversible change in cuticle permeability takes place when the insect or tick is exposed alternatively to high and low humidities. The water movements are the net result of two opposed processes, one active, the other passive. So far as is known, secretion tends constantly to move water inwards through the cuticle. When the force favouring passive evaporation is large, secretion can merely reduce the rate of water loss; when it is small or non-existent, secretion can result in water uptake.

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* The initial coefficients of asymmetry are based on extrapolation of the curves for evaporation rates.

Dr. H. Hurst (*Cambridge*) (*communicated*): In my paper, I have stressed the lipophylic nature of the epicuticular rods which act as a support for the extensible laminated lipo-protein.

Dr. D. J. Crisp (*Cambridge*) said: The movement of water in a direction in opposition to that of normal diffusion, which has been shown by Dr. Lees to take place in ticks, involves a gain in free energy which must be offset by some linked process where an equal or greater loss of free energy occurs. The suggestion of capillary condensation or of hygroscopic structures to adsorb water does not really help, because this water is still at a lower thermodynamic potential than that inside the insect, and a mechanism must be provided to withdraw it to a region of higher potential. There is no evidence at present as to what this process might be, but it must occur between the outermost cuticular layers and the body fluids; presumably, the hypodermal cells are responsible. In maintaining the outer cuticular layers in an unsaturated condition (i.e. at a higher osmotic pressure) than the body fluids, the behaviour is analogous to that of the protoplast wall described by Prof. Bennet-Clark,[9] and indeed to many other as yet unexplained mechanisms of secretion.[10] [11] [12] [13]

Dr. H. Hurst (*Cambridge*) said: Dr. Wigglesworth has shown that when the cuticle of a *Rhodnius* nymph is rubbed with alumina dust, the cuticle becomes more permeable to nicotine or rotenone, and the treated insects are affected more rapidly than the untreated control insects [1] The nicotine was used in aqueous solution, and the rotenone in powdered form. The conclusion was drawn that an abrasive dust increases the permeability of the cuticle to water and to insecticides by destroying the continuity of the superficial protective waxy layer.

I should like to draw attention to some experiments which suggest a different relationship between the desiccating action of a dust and the uptake of insecticides by the insect. A pyrethrum extract, in which the toxic principles are pyrethrins I and II, is used as the test insecticide. Adult *Tenebrio molitor* beetles, which possess hard waxy cuticles, are used as test insects. Fine alumina is used as the dust. The insects are allowed to walk on a thin film of pyrethrins deposited from a 0·1 % alcoholic solution on a glass surface. Within 5–8 min. the insects exhibit typical symptoms of pyrethrin intoxication and lose the power of co-ordinated movement. The poison has penetrated the protective lipid layer and attained a critical concentration at the peripheral nervous system which is associated with the cuticle framework.

When paralysed insects are covered with a thick layer of alumina, there is a gradual recovery of nervous co-ordination, and within 15–30 min, the insects are able to walk normally. If the dust is allowed to remain on the insects they begin to lose water by transpiration through the cuticle, and die within 8–12 hr. But during this stage there is no appearance of the symptoms of pyrethrin poisoning. The untreated insects remain paralysed. Both the dusted and the control insects have received equivalent dosages of pyrethrins, but the dust has clearly displaced pyrethrins from the peripheral nervous system. The

[9] Bennet-Clark (This Discussion).

[10] Höber, *Physikaliche Chemie der Zelle und der Gewebe* (Leipzig 1926).

[11] Keys, *Trans. Faraday Soc.*, 1937, **33**, 972.

[12] Kitching, *Biol. Rev.* 1938, **13**, 403.

[13] Adolph, *Physiological Regulations* (Lancaster 1943).

poison is insoluble in water, but soluble in fat solvents so that it must become localised or stored in the protective waxy layer. If the dust merely abraded the layer by a mechanical action which resulted in the production of local discontinuities in the wax layer, the effective storage capacity of this layer for pyrethrins should not materially change. In fact, pyrethrins I and II, which are capillary-active liquids forming a liquid-expanded monolayer at an air-water interface, should penetrate between the discontinuities into the underlying layers.[14] The sensory nerve endings of the peripheral network are not embedded in a superficial wax layer, but terminate distally beneath specially modified thin regions of the cuticle framework. The coincidence between the recovery from pyrethrin poisoning and the desiccating action of the dust suggests that there is an outward displacement of lipid containing dissolved pyrethrins from the cuticle framework. This is initiated by the adsorption displacement of lipid on to the dust surfaces from the superficial surface of the cuticle.

The above conclusion may be confirmed in the following ways :

(1) The paralysed beetles do not recover if treated with a wet dust. Neither is there any lethal desiccating action.

(2) Only dusts which exert a desiccating action show an " antidote " action on the initial stages of pyrethrin poisoning. In fact, desiccating action is directly proportional to " antidote " action. The order of decreasing desiccating activity of some typical powders is alumina > silica (Neosyl) > charcoal (blood) > calcium sulphate (Fygran) > talc > chalk. The order of decreasing " antidote " action on pyrethrin poisoning runs in the same direction. Finely divided tungsten powder, which can exert an abrasive and desiccating action when rubbed *hard* into the cuticle of insects, has neither desiccating activity nor does it induce recovery from pyrethrin poisoning, when lightly dusted on the insects or when these are allowed to crawl in the dust.

(3) The above results become of general significance in terms of competition between the surfaces of a dust and the bound lipo-protein framework of the epicuticle for the labile lipid components in which the pyrethrins are dissolved and presented to the peripheral nervous system.

In the system

Dust surface	epicuticle pyrethrins mobile lipids	peripheral nerve endings

the adsorption displacement of mobile lipid and pyrethrins is initiated by contact of the cuticle with the dry surfaces of the dust. Recovery does not take place if the dust is wet or if the paralysed insect is rotated at an air-water interface. If a paralysed insect is coated with a *thin* layer of alumina or silica dust and exposed to an increasing degree of humidity, recovery is only slightly delayed at relative humidities within the range 40 %–70 %. Within this range there is roughly a linear relationship between humidity and sorption of water by the dust. Recovery is either partial, or does not occur at humidities above 90 % or at saturation vapour pressures, when capillary condensation of water on the dust surfaces is a limiting factor.

In the above system the storage capacity of the thin layer of dust for pyrethrins is small. The following reversible sequence of events occurs when a paralysed insect coated with such a thin layer of dust is exposed to an alternation of humidity conditions. At low humidities (40 % ; 20° c.) the *Tenebrio* beetle recovers ; if the humidity is raised to saturation point, the insect becomes paralysed once more. When the humidity is lowered, the insect recovers. The sequence is, in fact, reversible, provided that the dosage of pyrethrins is adjusted so that the internal concentration at the central nervous system does not become a limiting factor. For example, if the beetles are paralysed by internal injection of pyrethrins, desiccating dusts exert no " antidote " action, even when dry.

From these simple experiments it is permissible to conclude that even with hard waxy cuticles, an adsorption displacement of labile lipid may be the primary cause of an increase in the rate of water loss through the cuticle. This leads to an associated outward displacement of oil-soluble insecticide which is stored in the lipids. We should also expect that water-soluble insecticides would pass more readily through the cuticle after adsorption displacement of mobile lipid by the dust. In Fig. 5*g*, of my contribution to this Discussion, I have shown that the waxy cuticle of a freshly moulted *Tenebrio* larva becomes permeable to catechol in aqueous solution after treatment with alumina The pattern of tanning is identical to that in the normal hardened cuticle, and there are no local abrasion marks. Here we have a displacement of labile lipid from a structural protein and associated phenoloxidase in the same way as there is a displacement of protective lipid from the peripheral nerve endings in the adult after treatment with alumina. These conclusions support Dr. Wigglesworth's observation that the activity of an aqueous solution of nicotine is increased after the cuticle is treated with a dust. The action is not due to mechanical abrasion, but to an exposure of the hydrated protein phase to the insecticide. Dr. Wigglesworth's experiments with the rotenone-alumina systems are less conclusive. He points out that normal insects were unaffected by dry powdered rotenone (90 %) at the end of 3 weeks; those rubbed with alumina dust before application of rotenone showed weakness in 8 hr. and were dead in less than 24 hr. In Table II of this original paper, Dr. Wigglesworth records that 5th stage nymphs of *Rhodnius* lose 46·5 % of the original body weight after treatment with alumina dust alone *within* 24 *hr.*[4] It is not clear, therefore, whether the lethal action in the insect treated with alumina and rotenone, is due to the alumina alone, or to the combined action of the components.

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[14] Hurst, *Trans. Faraday Soc.*, 1943, **39**, 390.

Dr. Wigglesworth has inferred from his experiments that the activity of insecticidal powders may be enhanced if an abrasive dust is incorporated with the filler, but he has produced no direct evidence in support of this conclusion. It is of interest to see whether we can foretell the probable action of a desiccating dust which is added to an impregnated pyrethrum powder.

In the system:

dust surface (d_1)	pyrethrin film (p)	Epicuticle mobile lipids (l)	peripheral nerve endings (n)

where a fine dust (d_1) is impregnated with a deposit (p) of pyrethrins, and uniformly distributed over the surface of the cuticle of an insect, the biological activity of (p) depends on the uptake and storage of (p) in the mobile lipids (l) and on the accessibility of this mixed lipid-pyrethrin "phase" to the peripheral nerve endings (n). Another important factor must be considered; this is the availability of pyrethrins which are partially immobilised on the dust surfaces by adsorption. A *Tenebrio* adult becomes paralysed within 5–8 min. when treated with a pyrethrum-chalk powder containing 0·4% pyrethrins, so that adsorption of pyrethrins by the dust is not a limiting factor. The chalk "filler" alone exerts no desiccating action on the insect even after prolonged contact. If a proportion of a desiccating dust is now mixed with the pyrethrum-chalk dust, contact of the desiccating dust component should result in adsorption displacement of (l) from the cuticle framework, so that the storage capacity of the lipids remaining in the epicuticle framework is decreased. In other words, the desiccating component should inhibit and not increase the activity of the pyrethrum-chalk dust. This is consistent with experimental observation. If 20 % alumina is incorporated in a pyrethrum-chalk dust, the effective concentration of pyrethrins is reduced by a factor of 0·8. But the mixed system becomes inactive against *Tenebrio* beetles. That this is not due to a simple diluent action of the alumina is shown by two experiments.

(1) If the mixed system is moistened with water, the beetles become paralysed, but recover partially or completely after the water has dried off.

(2) If 20–40 % chalk filler is added to the pyrethrum-chalk dust the insects are still paralysed within 10 min. Here the chalk acts as a simple diluent.

There is a direct relationship between the antagonistic action of desiccating dusts on pyrethrum-dust powders, the "antidote" action on paralysed insects, and the loss of water resulting from adsorption displacement of lipid. This relationship does not hold in the presence of water, and the fundamental factor involved is clearly a non-specific adsorption of lipid on to the crystalline surfaces of the dust. The evidence produced by Dr. Wigglesworth that "abrasive" action indicates a mechanical destruction of the superficial wax layer in the same way as abrasion with emery cloth results in a destruction of the layer is subject to criticism. An " abrasive " dust produces no visible sign of abrasion on the cuticle surface, a fact noted by Dr. Wigglesworth.[4] It is the inner epidermal cells which react as if they are " wounded." Coarse abrasion marks are seen after rubbing the surface of the cuticle with emery cloth. These may also be obtained if the surface of the emery cloth is wetted with water, and an insect treated in this way dies from desiccation. A wet dust is inactive ; neither does fine emery *powder* sprinkled on to an insect show appreciable abrasive or desiccating action. The true significance of the results obtained by the " abrasive " action of a dust lies in the implication that the adsorbed lipids are removed from the cuticle at the points of contact of the dust surfaces with the waxy layer. These lipids are not mobile on the dry dust surfaces to an appreciable degree. The inactivity of a wet dust shows that the asymmetrical field of forces resident at an air-water interface is insufficient to induce a reorientation and displacement of lipid from the cuticle, except at critical temperatures at which the mutual association between the labile lipids and the bound lipo-protein framework of the epicuticle is no longer a limiting factor in the competitive systems.

Dr. H. Hurst (*Cambridge*) said : Dr. Wigglesworth has described in detail the actions of dusts, detergents, such as sodium cetyl sulphate, and fat solvents such as chloroform on the permeability of the insect cuticle.[8] Permeability is measured in relation to the rate of evaporation of water through the cuticle. This rate is increased by all the reagents used and is attributed to an increase in permeability of the protective wax layer. Dr. Beament has shown that the permeability of waxed membranes is increased by similar treatments, and this is taken to be critical evidence that the structure of insect cuticle is analogous to the simple membrane systems.[5] I should like to refer to some experiments which I have carried out on insects with waxy and non-waxy types of cuticles. These experiments indicate that there are, in fact, fundamental differences between the mode of actions of a dust, a soap, and a fat solvent in relation to cuticle permeability.

With regard to the mode of action of a dust, I have already referred to the use of *Tenebrio* beetles as test insects. If the cuticle is painted with an alcoholic solution of pyrethrins (0·1 %) the insects become paralysed within a few minutes. The toxic principles obviously penetrate to the peripheral nervous system. If a mature *Calliphora* larva is treated in this way, symptoms of paralysis do not develop, but when the apparently normal insect is allowed to remain in contact with an untreated *Tenebrio* beetle, the latter insect becomes paralysed. Clearly there is a layer of pyrethrins on the surface of the *Calliphora* cuticle which does not penetrate into the bulk framework, but is taken up by the more susceptible insect. If the *Calliphora* larva is now painted with kerosene, or immersed in kerosene, paralysis develops in 1–2 min. The adsorbed layer of pyrethrins has penetrated through the epicuticle to the peripheral nervous system. This must be attributed to the presence of kerosene in the cuticle framework, or to a swelling action of kerosene on the lipid components. An aqueous solution of a soap, such as sodium cetyl alcohol, does not induce the penetration of pyrethrins through the cuticle. A dust, such as alumina or silica, has the reverse action and displaces the adsorbed layer from the cuticle.

Further evidence for a swelling action of kerosene on the lipids is given by comparison with a rubber membrane system. A thin rubber membrane, of the type used in toy balloons, is stretched over one end of a glass tube open at both ends. *Tenebrio* beetles are used as biological " indicators " for measuring the rate of passage of pyrethrins through the membrane. Two or three beetles are placed in the tube so that they walk on the internal rubber surface. The outer exposed rubber surface is painted with an alcoholic solution (0·5 %) pyrethrins. Even after exposure to the internal rubber surface for several hours, the beetles remain normal. When the outer surface of the rubber is painted with kerosene, the rubber membrane swells slightly, and within 10–20 min., the insects show marked signs of pyrethrin paralysis and are completely paralysed shortly afterwards. As with the living insect, a dust or aqueous soap solution does not induce the penetration of pyrethrins through the rubber membrane.

These experiments distinguish between the action of kerosene in increasing the permeability of the cuticle to pyrethrins, and the lack of sensitising effect shown by a dust and a soap. We can readily distinguish between the action of a dust and a soap in the following way. *Tenebrio* beetles are paralysed by contact with a film of pyrethrins on glass. I have already described experiments which show that treatment of the paralysed insects with alumina induces an outward adsorption displacement of lipid from the epicuticle framework resulting in the recovery of the insect. No recovery takes place when the insects are painted with an aqueous dispersion of sodium cetyl sulphate (5%), an aqueous dispersion of sodium oleate, or a thin film of lecithin.

It would appear that a common factor in the actions of a dust, a detergent, and a fat solvent is an increase in cuticle permeability to water, and the analogy with the waxed membrane systems is based entirely on *irreversible* increases in permeability, which can clearly be brought about by abrasive action, adsorption, detergent action or simple destruction of the layer by solution in fat solvents. It is only when we consider the properties of the lipids in relation to the passage of substances from outside into the insect, or when the penetrating substance remains immobilised or adsorbed in the cuticle, that more dynamic relationships between the structure, permeability, storage capacity, and association of the lipids with the supporting cuticle framework become apparent. The experiments which I have used to illustrate some of the principles outlined emphasise a point which is perhaps of particular significance in a general Discussion of this kind. It is the selection of biological material which guides the biologist in his attempts to elucidate biophysical principles. And it is the anomalous or aberrant biological systems which enable the biologist to select his biophysical principles.

Mr. R. Pal (*London*) said : I have been interested for some time in the wetting properties of insect cuticle and the factors concerned. The magnitude of the contact angle of a spray liquid is one of the major factors affecting the amount retained on an insect surface. When the contact angle is high, the droplet is nearly spherical and is likely to roll off the surface. On the other hand, when the contact angle is low, the drop has a larger area of contact and is therefore more stable and as a result more liquid is retained on the surface.

The measurements of contact angles of droplets at rest on a solid surface will give little indication of the behaviour when sprayed. The application of a spray is a dynamic process, during which the drops impact on the surface with a force and surfaces and interfaces are constantly being changed. The measurement of "static" angles of contact are therefore not an accurate criterion of the wetting and spreading ability of a liquid under the "dynamic" conditions existing when a spray is being applied.[15]

Thus there are two aspects of the problem to be considered :

(1) a new concept of contact angles under "static" and "dynamic" conditions, and

(2) the effect of impact force on the wetting and spreading of spray droplets.

(1) If we consider the advancing contact angle of drops of a liquid (*a*) when allowed to impact on a surface from a spray under considerable pressure, and (*b*) advancing over the surface when being continuously fed by a fine capillary tube. The contact angles will be different, although in both cases *advancing* contact angles will be obtained. On hitting the solid surface the droplet will spread out, due to mere force of impact, and give different values of *advancing contact angle provided the drop has not commenced to recede*. We have thus two different values of *advancing* contact angles for the same liquid on the same surface.

It will be clear, therefore, that in the study of insecticides we have to consider the *dynamic* contact angles of impinging droplets as opposed to *static* contact angles of drops involving no kinetic energy.

(2) The effect of impact force on the wetting and spreading of spray droplets was studied by allowing spray droplets of distilled water to impact on a standard beeswax surface. Simultaneous measurements of contact angles and the force of impact involved were measured. The following results were obtained.

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[15] Ben Amtoz and Hoskins. *J. Econ. Entom.*, 1937, **30**, 879.

	Advancing Contact Angle		
	Involving no Force of Impact.	When applied as a Coarse Spray.	When applied as a Fine Spray.
Contact angle of impinging droplets :	101°	100°	101°
Average drop size (diam.) ..	3 mm.	0·5 mm.	0·1 mm
Force of impact in ergs. ..	0	1·3–3·3	0·00019–0·035

From these figures it is evident that the contact angle of drops used in insecticidal spray (0·1 to 0·5 mm.) are not influenced by force of impact. When, however, drops of distilled water of larger size (5 mm. diam.) were allowed to fall from a capillary tube on to a standard beeswax surface from heights varying from 5 to 20 cm., there was a reduction in the magnitude of advancing contact angles.

In the spraying of plants or other surfaces where very coarse sprays are used, this phenomenon may be of considerable practical value. On incorporating "adhesives" in sprays the drops will on impact spread out over a larger area, thus not only will each drop cover a larger area, but will be retained on the surface thus increasing the total amount of spray deposit.

Drops allowed to Impact from a height of	Average Contact Angle in Degrees.
0 cm.	101
5 cm.	95
10 cm.	94
15 cm.	95
20 cm.	95

The second problem is concerned with the wetting properties of insect hairs.* I have been successful in measuring the contact angles formed by water and other liquids on these fine structures. The results obtained are summarized in Table I.

Both aqueous and oil sprays form finite angles. Distilled water formed an angle of 97·3°, methyl phthalate 52·8°, white oil 42·7° and odourless distillate 28·5°

TABLE I.—CONTACT ANGLES IN DEGREES OF VARIOUS LIQUIDS WHEN APPLIED TO HAIRS OF *Arctia caja L.*

	Advancing Angle.	Receding Angle.
Distilled water	97·3	90·2
Odourless distillate	28·5±1·0	25·3±0·8
Kerosene, non-aromatic ..	36·1±0·7	31·0±0·8
,, low aromatic ..	33·8±1·0	29·4±1·1
,, high aromatic ..	32·6±1·0	28·7±0·9
Spray oil	29·7±0·7	25·9±0·7
Shell A 12	35·8±1·0	31·2±1·2
Shell KB 30	39·0±1·0	24·7±0·9
P31 (White oil)	42·7±1·0	38·2±1·1
Malariol	41·1±1·01	35·1±1·0
Olive oil	31·6±0·78	28·0±0·8
Methyl phthalate	52·8±2·0	47·5±1·5

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* The cuticle of most insects is covered by scales and hairs and they determine to a large extent the behaviour of spray droplets when applied to insects. Tests were made on tiger moth larvæ (*Arctia caja L.*) whose relatively large hairs are easy to manipulate. The wetting of hairs of caterpillars does not give any indication of what happens on other insects but these studies were designed to obtain some tentative information about the wetting properties of these structures.

Dr. J. W. L. Beament (*Cambridge*) said: The breakdown in the water-proofing of the grasshopper egg involves only a small (hydropyle) area of the egg-shell. It may be noted that, towards the end of embryonic development (Beament 1948), the *Rhodnius* embryo secretes a fluid capable of removing (possibly as a fine emulsion) a wax from the inside of the shell layers. An insect embryo may very well be capable of de-waterproofing part of its shell by its own activities.

Dr. Slifer suggests that minute cracks may appear in the wax layer at low temperatures. It is at least certain that mechanical distortion of some egg-shells will cause cracks to appear in wax layers which, therefore, become more permeable. On the other hand, where adult insects swell, e.g. by taking a large meal of blood, there is no evidence to show that this occasions an increased permeability of the wax layer on the cuticle.

Mr. R. Pal (*London*) said: I have chanced to make an observation, at present unexplained, which may throw light on the penetration of liquid-water through insect cuticle.[16]

The leg of cockroach (*Periplaneta americana*) is transparent, and it is easy to observe the main trachea through the cuticle. If a drop of water is placed on the exterior of the leg, over this trachea, minute droplets appear almost immediately in the trachea. In all cases the droplets only appear in the length of the trachea covered by the drop on the cuticle. These droplets later coalesce, and if the water drop on the outside of the leg is allowed to evaporate they eventually also disappear. The droplets do not wet the intima of the trachea and are judged to consist mainly of water.

The droplets which form in the trachea do not appear to be due to cooling or condensation of water vapours in the trachea, as a result of evaporation of the drop on the surface. Nor it appears, is it due to any osmotic effect. This phenomenon might be due to penetration of liquid-water through the cuticle, if one could postulate such a possibility.

The cuticle of *Rhodnius* is also transparent and it is easy to observe the dorsal abdominal trachea, and similar droplets can be produced by applying water externally.

Dr. T. Swarbrick (*The Hague*) said: Several speakers have mentioned the use of paraffin in their experiments. Great care is necessary in drawing anything other than limited conclusions from these experiments since hydrocarbon oils of petroleum origin may vary considerably in their molecular species, although they may conform to the same standards as regards viscosity, boiling range and unsulphonatable mineral residue. Such oils may have very different "spreading pressures," so that on a standard surface they spread at different rates and to different degrees. It is also known that the presence of small amounts of impurities, particularly if these are strongly polar, will modify the spreading pressure of the oil on a water surface. This fact is now used as a basis for the production of high-spreading antimalarial oils which can be used at very low dosage per acre of water surface, because they spread out into such relatively thin films.

Dr. V. B. Wigglesworth (*Cambridge*) (*communicated*): Dr. Crisp in his paper has raised the question of the mechanism by which air first appears in the plastron. This is the same problem as the first appearance of air in the tracheal system, which may occur in some aquatic insects while they are still submerged. This probably takes place at the time when the waxy lining of the tubes is secreted and the adhesion of water so reduced that gases are liberated from solution. In discussing this problem in an earlier publication[17] reference was made to a simple experiment devised by Prof. N. K. Adam. Ordinary tap water is allowed to stand in two beakers, one thoroughly freed from grease with chromic acid, the other lined with paraffin wax. Bubbles of gas are soon liberated in the waxed beaker (at room temperature and atmospheric pressure) but not in the clean beaker.

Dr. W. H. Thorpe (*Cambridge*) said: On the screen are shown some ultra-violet photomicrographs of sections of the plastron bearing cuticle of the aquatic insect *Aphelocheirus æstivalis*. These photographs have already been published.[18] This technique was employed merely to provide increased resolving power and thus enable more accurate measurement of minute cuticular hairs than is possible by the ordinary light microscope. It was found incidentally, however, to reveal structures in the epicuticle which could not be observed by any other method and it seems that the technique may prove a useful one for cuticular studies generally. It will be seen that the plastron hairs are apparently continuations of structures within the exocuticle. These "roots" are seen to pass through several horizontal layers five or six of which appear to constitute the epicuticle and, with increased exposure, others are faintly visible in the outer region of the exocuticle. Little is known of the physical properties or chemical nature of the epicuticle of this insect but the fact that these structures absorb ultra-violet radiation more strongly than their surroundings suggests a protein framework. It will be seen that very superficially these photographs present a picture recalling the mosaic structure postulated by Dr. Hurst; though the layers are obviously much too thick ($1/20\mu$, 400A.) to be identified with Hurst's lamellæ Neither can they represent the four layers of epicuticle postulated by Dr. Wigglesworth. It seems therefore that these photographs cannot be regarded as giving any *detailed* support for either of the two main viewpoints represented in this Discussion. But even though the layers are not identifiable with any hitherto-recognised lamellæ, they do indicate the reality of some kind of transverse orientation and the technique may eventually provide a clue for the further elucidation of cuticular structure, and it may eventually prove possible to correlate the facts here given with some extention or development of existing theories.

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[16] Pal, *Nature*, 1947, **159**, 400.

[17] Sikes and Wigglesworth, *Quart. J. Micro. Sci.*, 1931, **74**, 165.

[18] Plate 6, Thorpe and Crisp, *J. Expt. Biol.*, 1947, **24**, 227.

IV. PERMEABILITY TO WATER AND WATER VAPOUR OF TEXTILES AND OTHER FIBROUS MATERIALS

Introductory Paper

BY A. B. D. CASSIE

Received 23rd March, 1948

Three problems are covered in the papers of this section: the diffusion of a temperature or water-vapour concentration change through a porous and absorbing material, the steady diffusion of water through the same material, and finally the penetration of liquid water through the pores. They are all very much classical physics problems, and their recent serious discussion is due to their technical importance for such everyday materials as textiles, leather, and wood.

The diffusion of temperature or water-vapour concentration changes occurs in the processing of any water-absorbing material, and in the use of clothing made from hygroscopic fibres.[1] Theoretical discussion of this problem was much retarded by the general impression that water required a considerable time to diffuse from the surface to the interior of a fibre, and when it was shown that this time was so small that fibres could always be regarded as in equilibrium with the air immediately surrounding them,[2] progress became rapid and easy. This result provides the essential link that makes the theory manageable; for it means that the large weight of water absorbed by the fibres is available to control the water-vapour content of the atmosphere around the fibres ; or the water content of the fibres controls the conditions of diffusion. During any short interval in the diffusion, the moisture content of the fibres may be taken as constant, and this imposes the condition that the relative humidity of the air in the interstices between the fibres must remain constant. Suppose then, that the change is a decrease in temperature ; this tends to increase the relative humidity, and the fibres absorb water vapour tending to maintain the constant relative humidity ; in absorbing water vapour, the fibres evolve heat of absorption which tends to decrease the temperature change. The absorption of water vapour must be sufficient to give a decrease of vapour pressure which with the check in the drop of temperature maintains a constant relative humidity in the air. It is the maintenance of constant relative humidity that gives the very close coupling of temperature and water vapour which is discussed in Dr. Henry's paper.

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[1] Cassie, *J. Text. Inst.*, 1940, **31**, T17.
[2] King and Cassie, *Trans. Faraday Soc.*, 1940, **36**, 445.

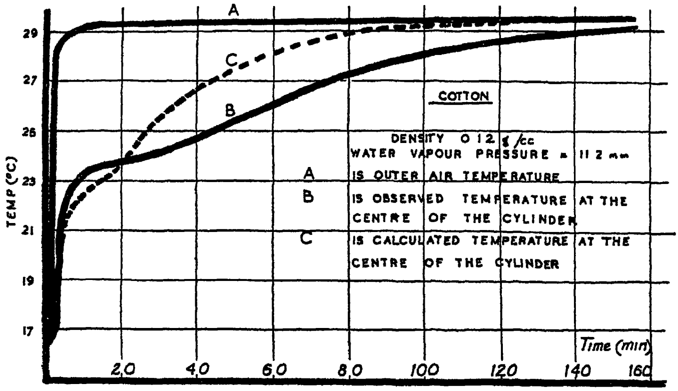

FIG. 1.—Diffusion ot temperature change through cotton.

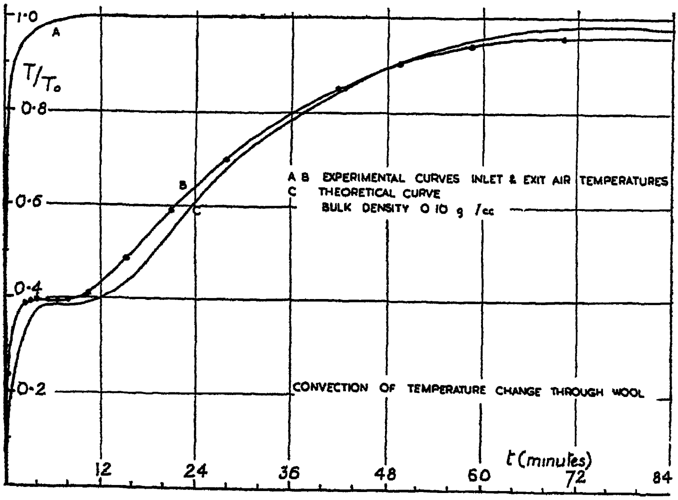

FIG. 2.

The success of this theory and of the corresponding theory for air forced mechanically through a mass of fibre is shown in Fig. 1 and 2. In both examples the mass of fibre was in the form of a cylinder, and a change of air temperature, without change of water-vapour concentration outside the cylinder was followed at the centre of the cylinder. The experimental curve of Fig. 2 was obtained by forcing air mechanically from the outside of the cylinder through the fibres to a central porous tube which enabled the air to escape. Theory[3] and experiment agree rather better for the mechanical movement of air than for the case of pure diffusion ; the observed temperature change for pure diffusion occurs more slowly than that predicted by theory. This discrepancy might be due to neglecting the time for diffusion from the surface to the interior of the fibres, but if this were true, an even larger difference between theory and experiment would be expected for air forced mechanically through the cylinder where the time scale of the process is much shorter. The discrepancy for the case of diffusion is much more likely to be due to the use of incorrect diffusion and diffusivity coefficients ; the values used were those for air, and the papers by Dr. Conmar Robinson *et al.* and by Dr. Stamm show that much more complex diffusion coefficients should have been used.

It might be possible to find a better fit of the curves of Fig. 1 by adjusting the diffusion coefficients, and at the same time obtain estimates of their true values, but much more reliable values are obtained from measurements of steady-state diffusion, such as are given by Robinson *et al.* and by Stamm. The interpretation of diffusion coefficients for absorbing materials is, however, very complex as may be judged from Stamm's work. Robinson *et al.* assume that the diffusion is entirely through the air spaces between the fibrils and this simple interpretation appears to be reasonably complete for leather. Pierce, Rees and Ogden,[4] and Baxter[5] have made similar measurements for textile materials and they find that diffusion through the water-absorbing fibres cannot be neglected. The problem is then to find an expression for the overall diffusion coefficient of a heterogeneous material. The same problem arises in heat conduction through heterogeneous materials, and although it has been discussed since the time of Stefan, no wholly satisfactory expression has been given. Baxter[5] has examined various formulæ that have been proposed for heat conduction, and so far as textiles are concerned, he finds that both heat and water-vapour diffusion data are best represented by Stefan's formula, which for diffusion coefficients may be written :

$$D = 0{\cdot}33(D_aV_a + D_fV_f) + \frac{0{\cdot}67\,D_aD_f}{D_aV_f + D_fV_a} \quad . \quad . \quad (1)$$

where D is the overall diffusion coefficient for a heterogeneous material with fractional volumes V_a and V_f with diffusion coefficients D_a and D_f respectively. Eqn. (1) is derived by assuming that the components are divided into slabs, one third of which lie parallel to the direction of diffusion, and two thirds normal to this direction.

When applied to measurements on wool fabrics, this equation gives values of D_f that are in reasonable agreement with those obtained from diffusion measurements for horn, which is closely similar to the material of wool fibres. Fig. 3 shows some empirical data together with curves for eqn. (1) and for Penman's relation[6] :

$$D = 0{\cdot}67D_aS, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where S is the porosity of the material. Penman's relation does not apply at bulk densities less than 0·4 g./cc. for wool, and few wool fabrics exceed this density. It is worth noting, however, that Penman's relation and eqn. (1) do not differ very greatly in the range of bulk densities 0·4 to 1·0 g./cc. Robinson's data are for bulk densities entirely within this range, and they would presumably fit either relation.

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[3] Daniels, *Trans. Faraday Soc.*, 1941, **37**, 506.

[4] Pierce, Rees, and Ogden, *J. Text. Inst.*, 1945, **36**, T169.

[5] Baxter, *J. Textile Inst.*, 1946, **37**, T39.

[6] Penman, *J. Agric. Sci.*, 1940, **30**, 437.

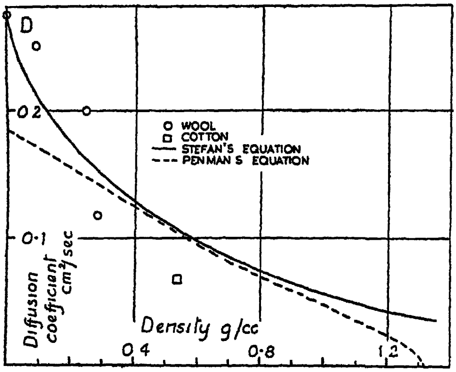

FIG. 3.—Density against diffusion coefficient.

The third question raised in the papers of this section is that of penetration of liquid water through pores. There is a little known geometrical theorem that has much bearing on this problem for textiles, and it is probably worth while drawing attention to it. A proof has been given previously.[8] The theorem states that the minimum radius of curvature R, of a circle which intersects two circles of radius r with centres $2(r + d)$ apart so that the tangents at the points of intersection make an angle θ, is given by:

$$R = r\cos\theta + \sqrt{(r + d)^2 - r^2\sin^2\theta} \quad . \quad . \quad . \quad (3)$$

The importance of this theorem may be seen from Fig. 4. If A and B are two cylinders, such as textile fibres or yarns, and water is forced between the two cylinders in the downward direction, the pressure required for penetration will be given by γ/R, where γ is the surface tension of water, and θ in eqn. (3) is the advancing contact angle, θ_A, for the cylinder surface and water. If a square pore is under consideration, the penetration pressure will be $2\gamma/R$.

The penetration pressure given by these relations is quite different from that obtained by the usual procedure of regarding the pore as a cylindrical capillary; in particular, there is no change in sign of the penetration pressure as the contact angle passes through 90° so that this angle does not divide the cylinders into wettable and water-repellent systems. The penetration pressure is, in fact, positive for any finite contact angle and a wettable textile fabric must have a fibre-water advancing contact angle that is zero.

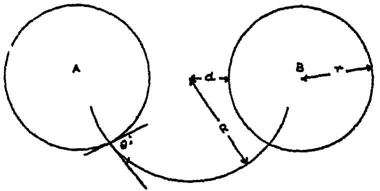

FIG. 4.—Geometrical theorem.

In view of this deduction, it may seem surprising that the data given in Bartell, Purcell, and Dodd's paper appear consistent, for they have regarded the pores between yarns as cylindrical capillaries. Their results are consistent because the contact angles for Finol and alcohol are zero, and the maximum air pressure required to expel the liquid will be $2\gamma/d$ for a square pore.

The large values and apparent insensitivity of the yarn contact angles given by Bartell *et al.* are due to the pronounced effect of yarn structure[7] on this angle; in fact, if the fibre-water contact angle is finite, the yarn and water contact angle is usually large because of the high porosity of yarns, and the observed values are characteristic of the yarn structure rather than of the fibre-water contact angle. It follows, therefore, that comparable cloths which must have comparable yarns, will show similar yarn-water contact angles, provided that all the fibres have finite contact angles.

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[7] Baxter and Cassie, *J. Text. Inst.*, 1945, **36**, T81.

This aspect of the water repellency of textiles is very similar to the phenomena discussed by Robinson *et al.* for leather; they also discuss the problem of receding contact angles and their conclusions are immediately applicable to textiles. The decay of the receding contact angle on exposure to water is the factor that ultimately determines the rain resistance of fabrics, and although a large advancing contact angle usually implies a slow decay of receding angle, the two do not necessarily follow one another.

THE DIFFUSION OF MOISTURE AND HEAT THROUGH TEXTILES

By P. S. H. Henry

Received 1*st March*, 1948

The General Case

In a previous paper by the author,[1] it was shown that whenever moisture diffuses through a porous absorbent body the thermal effects accompanying the process result in a coupled diffusion of moisture and heat which is mathematically analogous in many respects to a pair of coupled vibrations. Somewhat similar phenomena were described in a set of three papers by Cassie and others,[2] though they were concerned not so much with diffusion as with the flow of air through a porous body under the influence of a pressure gradient, and the resulting transfer of heat and moisture. All papers had textile materials in view, but the treatment would apply to any inhomogeneous absorbent material.

In the author's paper it was shown that the combined diffusion processes can be considered mathematically as equivalent to the independent diffusion of two quantities, each of which is a linear function of both vapour concentration and temperature. These quantities correspond to the "normal co-ordinates" of the well-known coupled vibration problem. The diffusion constants appropriate to these quantities are always such that one is greater and the other less than either of the diffusion constants which would be observed for the moisture and heat, were these not coupled by the interaction. The slower diffusion constant can never, however, become less than half the "isothermal" diffusion constant for moisture (D), or the "constant-vapour concentration" diffusion coefficient for heat ($\mathbf{D}$), whichever is the less.

The coefficient for the faster "normal co-ordinate" may be many times either D or $\mathbf{D}$, and may approach the "adiabatic" diffusion coefficient for moisture (D'), or the "no vapour diffusion" coefficient for heat ($\mathbf{D}'$), whichever is the faster. The diffusion constants D, D', $\mathbf{D}$, $\mathbf{D}'$ were defined in the author's paper mentioned above. Since in practice it is not possible to prevent interaction between the thermal and vapour diffusions, these constants cannot be measured directly, but they enter into the theory which is required to predict how the combined diffusion will be affected by various circumstances.

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[1] Henry, *Proc. Roy. Soc. A*, 1939, **171**, 215.

[2] Cassie, King, and Baxter, *Trans. Faraday Soc.*, 1940, **36**, 445, 453, 458.

The diffusion of the normal co-ordinates cannot be observed directly, but could be deduced from measurements of vapour concentration and temperature at various points and times. If interest is centred on the diffusion of moisture it appears as if the latter can be divided into two parts which diffuse independently at different rates.

Diffusion Rates

In eqn. (22) of the paper referred to, it is shown that if the diffusion coefficients of the two normal functions are written $1/\mu_1^2$, and $1/\mu_2^2$, then μ_1^2 and μ_2^2 are the roots of the equation,

$$\left(\mu^2 - \frac{1}{D}\right)\left(\mu^2 - \frac{1}{\mathbf{D}}\right) = \frac{\lambda\nu}{D\,\mathbf{D}} \quad . \quad . \quad . \quad (1)$$

where λ and ν are certain constants expressing the degree of coupling (see the last half of this paper). If we write $1/\mu_1^2 = D_1$ and $1/\mu_2^2 = D_2$ in order to preserve the representation of a diffusion coefficient by the letter D, and if we define D_1 as that root which tends towards D as the coupling (as measured by $\lambda\nu$) tends to zero, and D_2 as that which tends towards $\mathbf{D}$, then we have

$$D_1 = \frac{2D\,\mathbf{D}}{D + \mathbf{D} + \sqrt{(\mathbf{D} - D)^2 + 4\lambda\nu D\,\mathbf{D}}} \quad . \quad . \quad (2)$$

$$D_2 = \frac{2D\,\mathbf{D}}{D + \mathbf{D} - \sqrt{(\mathbf{D} - D)^2 + 4\lambda\nu D\,\mathbf{D}}} \quad . \quad (3)$$

If we put $\frac{D}{\mathbf{D}} = u$, these can be written

$$\frac{D_1}{D} = \frac{2}{u + 1 + \sqrt{(1 - u)^2 + 4u\lambda\nu}} \quad . \quad . \quad (4)$$

$$\frac{D_2}{D} = \frac{2}{u + 1 - \sqrt{(1 - u)^2 + 4u\lambda\nu}} \quad . \quad . \quad (5)$$

Fig. 1 shows a nomogram for solving both these relations. If a straight line (such as a stretched thread) be placed so as to cut the two straight scales at the appropriate values for u and $\lambda\nu$, then the points at which it cuts the circular scale give D_1/D and D_2/D respectively. To find $D_1/\mathbf{D}$ and $D_2/\mathbf{D}$ it is merely necessary to use $1/u$ in place of u. It is usually convenient to express D_1 in terms of D and D_2 in terms of $\mathbf{D}$.

If the coupling is weak—i.e., if $\lambda\nu$ is small compared with unity—then

$$\frac{1}{D_1} \sim \frac{1}{D} + \frac{\lambda\nu}{\mathbf{D} - D} \rightarrow \frac{1}{D} \text{ as } \lambda\nu \rightarrow 0 \quad . \quad . \quad (6)$$

$$\frac{1}{D_2} \sim \frac{1}{\mathbf{D}} - \frac{\lambda\nu}{\mathbf{D} - D} \rightarrow \frac{1}{\mathbf{D}} \text{ as } \lambda\nu \rightarrow 0 \quad . \quad . \quad (7)$$

so that D_1 and D_2 tend towards D and $\mathbf{D}$ respectively as the coupling tends to zero.

If however the coupling is strong—i.e., $\lambda\nu$ is nearly equal to unity, as happens in many applications to textile materials—we get the following approximations.

$$D_1 \sim \frac{D\,\mathbf{D}}{D + \mathbf{D}} + (1 - \lambda\nu)\,\frac{D^2\mathbf{D}^2}{(D + \mathbf{D})^3} \rightarrow \frac{D\,\mathbf{D}}{D + \mathbf{D}} \text{ as } 1 - \lambda\nu \rightarrow 0 \quad (8)$$

$$\text{and } D_2 \sim \frac{D + \mathbf{D}}{1 - \lambda\nu} - \frac{D\,\mathbf{D}}{D + \mathbf{D}} \rightarrow \frac{D + \mathbf{D}}{1 - \lambda\nu} \text{ as } 1 - \lambda\nu \rightarrow 0 \quad (9)$$

The approximations (8), (9), and one or other of (6) and (7) also hold if D and $\boldsymbol{D}$ are of widely different magnitudes whatever the value of $\lambda\nu$.

Approximation (8) may be written

$$\frac{1}{D_1} \rightarrow \frac{1}{D} + \frac{1}{\boldsymbol{D}} \quad \text{as } 1 - \lambda\nu \rightarrow 0 \quad . \quad . \quad . \quad (10)$$

It will be seen that D_1 is always rather less than whichever is the smaller of D and $\boldsymbol{D}$, and is more nearly equal to one or other of these the greater is the disparity between D and $\boldsymbol{D}$. If the latter are equal, D_1 is equal to half of either of them, this being the greatest divergence possible.

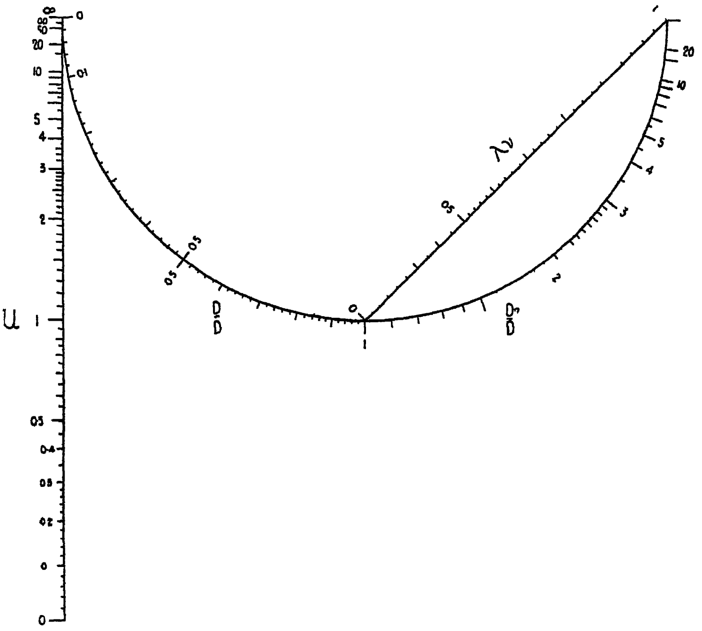

FIG 1 —Nomogram for D_1/D and D_2/D in terms of u and $\lambda\nu$

Eqn. (16) of the author's original paper shows that $(1 - \lambda\nu)$ is equal to the ratio between the isothermal and adiabatic diffusion coefficients for the vapour, and also to the ratio between the "constant-vapour concentration" and "no vapour diffusion" coefficient for the diffusion of heat. Hence approximation (9) can be written

$$D_2 \rightarrow D' + \boldsymbol{D}' \quad \text{as} \quad 1 - \lambda\nu \rightarrow 0 \quad . \quad . \quad . \quad (11)$$

Thus if D' and $\boldsymbol{D}'$ are widely different D_2 approximates to either the adiabatic vapour diffusion coefficient or the "no vapour diffusion" thermal diffusion coefficient, whichever is the greater. When D' and $\boldsymbol{D}'$ are comparable, D_2 is greater than either, showing that the second "normal function" diffuses faster than either vapour or heat would if the diffusion of the other could be stopped. This conclusion seems surprising at first, but we shall see in the next section that a rapid passage through the material of a change in C—the concentration of vapour in the pores—does not necessarily mean a rapid transference of moisture, but may be produced by a change in its distribution as between solid and pore space. The bulk of the actual moisture transfer proceeds at the slow rate of the first normal function.

Amplitudes

For simplicity let us confine our attention to the diffusion which occurs when a body at equilibrium with one set of external conditions is suddenly transferred to another set of conditions. Moisture and heat will diffuse in or out until the body comes into equilibrium with its new surroundings. Further, let us suppose that no change is made in the external temperature, only the external humidity being changed. Referring to eqn. (35) of the original paper, we can therefore put $\Delta_0 T = 0$. Substituting also $1/D_1$ and $1/D_2$ for μ_1^2 and μ_2^2 respectively, and rearranging, we get for the ratio of the change in C at any instant to the equilibrium value of the change:

$$\frac{\Delta C}{\Delta_0 C} = \frac{D_1 (D_2 - D) f_1 - D_2 (D_1 - D) f_2}{D (D_2 - D_1)} \quad . \quad . \quad (12)$$

Here f_1 and f_2 are the functions of position and time appropriate to the particular diffusion problem concerned. They differ only in their time-scale, since f_1 and f_2 assume the diffusion constants D_1 and D_2 respectively, but are otherwise identical. In the case we are considering, both start at zero and increase towards unity as the system approaches equilibrium.

Eqn. (12) can be written

$$\frac{\Delta C}{\Delta_0 C} = (1 - p) f_1 + p f_2 = f_1 + p (f_2 - f_1) \quad . \quad . \quad (13)$$

where

$$p = \frac{D_2 (D - D_1)}{D (D_2 - D_1)}.$$

Thus we may consider the diffusion process as consisting of two " waves," f_1 and f_2, which proceed independently at different rates, and whose final amplitudes add up to give the value for ΔC necessary for eventual equilibrium. Alternatively, especially when p is small (as it often is), we may take the right-hand form of (13) and consider the process as consisting of a " main wave," f_1, which proceeds steadily towards equilibrium, disturbed by the " temporary wave " $(f_2 - f_1)$, which increases to a maximum and then decreases to zero again.*

It will be seen from (13) that p is a dimensionless quantity that can be expressed in terms of the ratios D_1/D and D_2/D. Since we have already seen that these can be calculated from the value of u $(= D/\boldsymbol{D})$ and of $\lambda\nu$ only, it follows that p can also be calculated directly from u and $\lambda\nu$. In fact the relation can be written

$$(2p - 1)^2 = \frac{(u - 1)^2}{(u - 1)^2 + 4u\,\lambda\nu} \quad . \quad . \quad . \quad (14)$$

A nomogram for calculating p in terms of u and $\lambda\nu$ is shown in Fig. 2. It will be noticed that the right-hand side of (14) is unaltered if $1/u$ is substituted for u. Hence the scale for u from 1 to ∞ enables all possible values of u to be dealt with. It also follows from this symmetry that the same numerical value for p can be used for calculating the relative values of the two " waves " when it is the external temperature rather than the humidity which has been altered.

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* The appropriateness of this latter conception has been called in question by Cassie (loc. cit.), but the author wishes to point out that the division into components of any additive phenomenon (such as the simultaneous diffusion of our normal functions) is a purely arbitrary process. Any one method of choosing the components is as valid as any other. Examples are the resolution of forces into components, which can be done in many different ways, and representation of the transmission from a broadcasting station either as a modulated wave of constant frequency, or as a carrier wave plus side bands of different frequencies.

In practical problems concerning the diffusion of moisture into, or out of, porous bodies it is usually not the value of C, the concentration of vapour in the pores, which is of interest, but the total amount of moisture, absorbed or free, per unit dry mass of the porous body. Since this is affected both by C and by the temperature, we cannot use (13) to calculate the progress of the diffusion. The appropriate calculation was carried out in the author's original paper and the results expressed in eqn. (40) and (42) thereof. The latter is in the most convenient form for our purpose, and is a good approximation for all the more absorbent textiles. Putting $\Delta_0 T = 0$ in (42), therefore, we get, where M is the moisture content of the material, and $\Delta_0 M$ is the final value of the change in it:

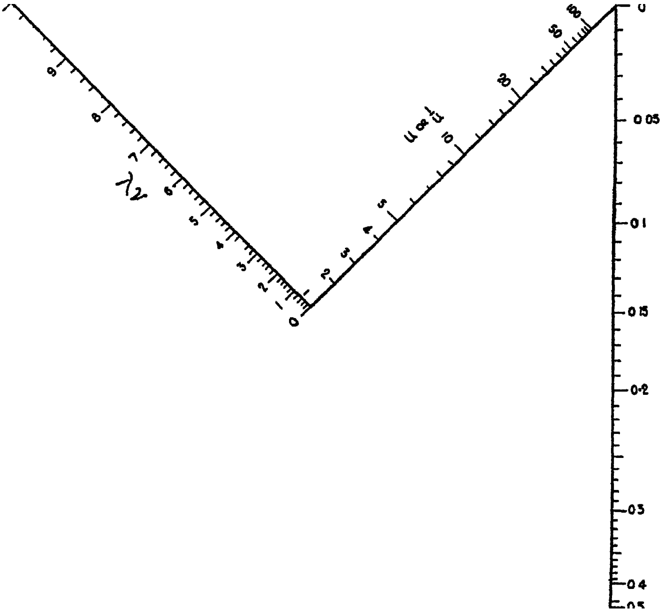

FIG. 2.—Nomogram for p in terms of u and $\lambda\nu$.

$$\frac{\Delta M}{\Delta_0 M} \backsim f_1 - \frac{u^2 (f_2 - f_1)}{(1+u)^2 (1+\varepsilon\omega) + u} \quad . \quad . \quad (15)$$

$$\backsim f_1 - n(f_2 - f_1), \quad \text{or} \quad (1+n) f_1 - n f_2,$$

$$\text{where } n = \frac{u^2}{(1+n)^2 (1+\varepsilon\omega) + u}.$$

Note the negative sign of the secondary wave in this case, indicating an initial slowing-down of the moisture transfer. A nomogram for calculating n in terms of u and $1 + \varepsilon\omega$ is shown in Fig. 3. It may be pointed out that, under the same conditions,

$$1 + \varepsilon\omega \backsim \frac{1}{1 - \lambda\nu} \quad . \quad . \quad . \quad . \quad . \quad (16)$$

Application to Cotton

To illustrate numerical application of the theory we will calculate the way in which we should expect the rate of diffusion of moisture into, or out of, a package of raw cotton to depend upon the temperature and the average humidity during the process. It will be realised that in applying a theory like this to a body as complex in structure and properties as a cotton package, many approximations have to be made, and the result can only be claimed to give the probable order of magnitude of the effects. The final test must be that of experiment. None the less, the calculation is worth carrying out, quite apart from its theoretical interest, because experimental determinations of diffusion rates are usually a lengthy business, and to examine thoroughly the combined effects of the three variables—temperature, humidity and density—even on one material only, without a theoretical background to guide the experiments, would involve more time and labour than would be worth while.

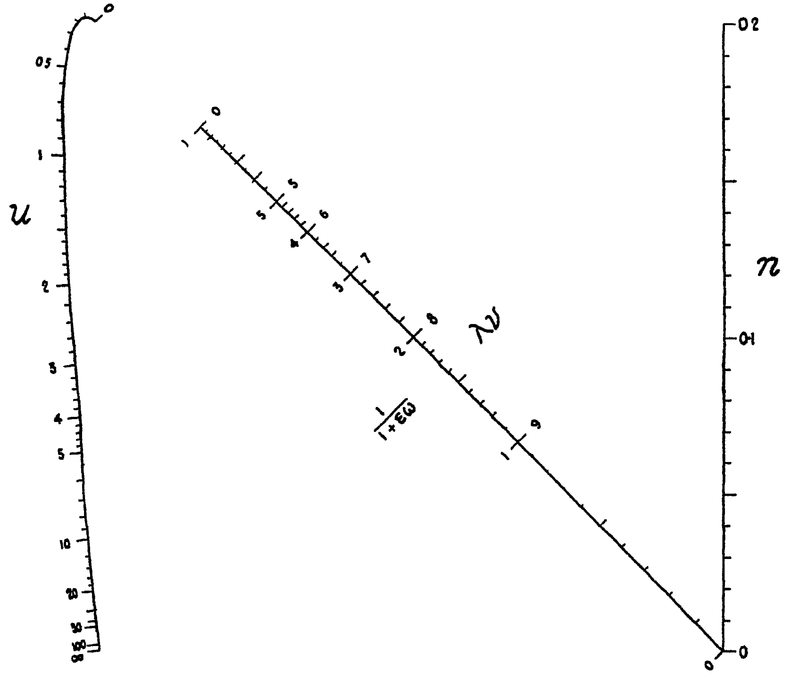

Fig 3 —Nomogram for n in terms of u and $\lambda\nu$ or $1/(1+\varepsilon\omega)$

Some effects that we shall be neglecting, amongst others, are the following. (1) The non-linear nature of the relation between the amount of moisture absorbed by cotton and the concentration of the water vapour in equilibrium with it. (2) The hysteresis in the moisture absorption. (3) The change in structure of the material due to swelling as the cotton absorbs moisture.

Fortunately, in the case of cotton the first approximation is quite good over the middle range of humidities, since the relation is not far from linear between relative humidities of 10 % and 70 % (see Urquhart and Williams[3]). Outside these limits, the calculations can only be regarded as applying to small changes. Neglect of hysteresis is, in practice, a much more serious, but unavoidable, source of error. Though plenty of data exist for the moisture relations of cotton that starts in the dry state and absorbs moisture steadily till it reaches 100 % R.H., and also for cotton that starts at 100 % R.H. and

[3] Urquhart and Williams, *J. Text. Inst.*, 1924, 15, T559.

loses moisture steadily, the author has not seen any published work dealing with small humidity cycles except in the case of wool (Speakman [4]). It is certain that the slopes of the characteristic curves in such cycles may differ very greatly from those given by large cycles. The calculations given below are based on Urquhart's data for cotton absorbing moisture and starting at the dry state. They must therefore be taken as applying only to this case, though there will not be much error in using them for cotton that starts damp and is losing moisture, since we shall be concerned only with the *slope* of the characteristic curves. The change in structure due to swelling of the cotton fibres does not lend itself to calculation, but would probably give rise to serious error only with very dense packages.

It will be noticed that none of the quantities discussed below, except the diffusion coefficients, contains the element of time in their dimensions. As a matter of fact, time effects other than those concerned in simple diffusion have been ignored in the assumptions made. For instance, the rate of attainment of equilibrium of a cotton hair with the water vapour immediately surrounding it is supposed to be instantaneous, or at least very rapid compared with the other processes concerned. Existing evidence on this point is conflicting, but it seems likely that whilst most of the change takes place very rapidly, there is a slow alteration produced in the cotton itself by changes in humidity which leads to a slow continued uptake or loss of moisture over a period of days. If this effect turns out to be of importance, the size of the package will take more than a purely geometrical part in the process.

Observed Quantities.—Below are listed the experimental data on which the calculations to follow are based. The symbols used throughout are those of the author's original paper, except that k and q have been substituted for κ and k respectively in order to conform with the Recommended List of Symbols.

Specific properties of cotton, not dependent upon the density of the package, are as follows.

ρ_S, the effective density of the cellulose, reckoned as g. *dry* cellulose per cc. of space occupied by the cotton hairs. According to Davidson,[5] the apparent specific volumes of cotton cellulose in toluene and in water are of the order 0·65 and 0·625 cc./g. respectively. This difference of about 4 % can be neglected for our purposes, and we will take the volume of the moist cellulose to be the sum of those of the dry cellulose and of the water. Accordingly, if M g. water are absorbed by 1 g. cellulose, we can take

$$\rho_S = 1/(0{\cdot}63 + M) \text{ in g./cm.}^3 \quad . \quad . \quad . \quad (17)$$

D^* is the diffusion coefficient for water vapour through air. In I.C.T., it is given as $0{\cdot}220\left(\frac{T}{273}\right)^{1\cdot75}$ cm.^{2}/sec. at an atmospheric pressure of 760 mm. Hg.

σ, defined as $\left(\frac{\partial M}{\partial C}\right)_T$, is the rate at which the moisture content of the cotton (expressed as a fraction of the dry weight) increases as the concentration of water vapour in equilibrium with it rises, the temperature remaining constant. It can be shown that it is equal to $\frac{RT}{MP_0}\left(\frac{\partial M}{\partial r}\right)_T$, where M is the mean molecular weight of water vapour under the given conditions, in g./mole; P_0 is the equilibrium vapour pressure of water at T°K. in mm. Hg.; and r is the R.H. expressed as a fraction (i.e., not as a percentage). Values for $\left(\frac{\partial M}{\partial r}\right)_T$ were obtained from the results of Urquhart and Williams.[3] Fig. 4 shows σ in cm.^{3}/g. plotted logarithmically against R.H. for various temperatures.

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[4] Speakman, *J. Text. Inst.*, 1936, **27**, T183.

[5] Davidson, *J. Text. Inst.*, 1927, **18**, T175.

ω, defined as $-\left(\frac{\partial M}{\partial T}\right)_\sigma$, is the rate at which the moisture content of the cotton decreases as the temperature increases, the concentration of the vapour remaining constant. This quantity, also, can be obtained from the

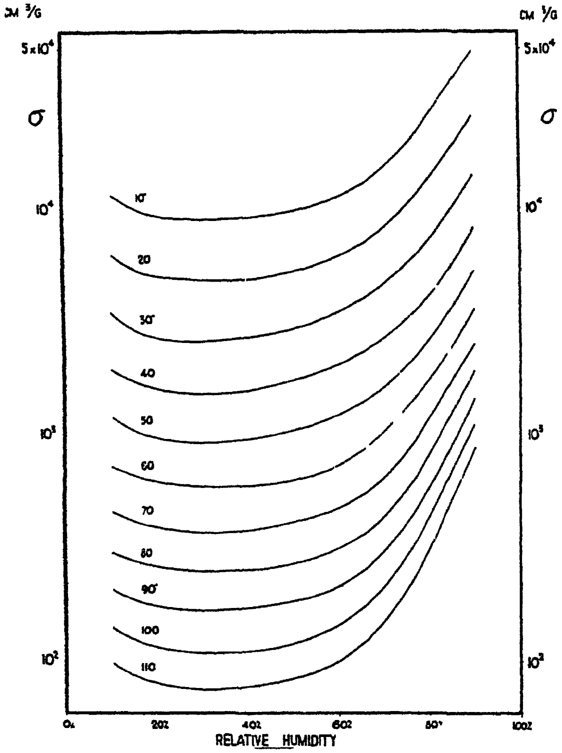

FIG. 4.—σ plotted logarithmically against relative humidity for various temperatures.

data of Urquhart and Williams.[3] It can be shown that ω is equal to $-\frac{MrP_0\sigma}{RT^3}\left\{\frac{\partial \log (P/T)}{\partial (1/T)}\right\}_M$, which is a convenient form because Urquhart and Williams plot log (P/T) against $1/T$, getting straight lines whose slope is easily measured. Fig. 5 shows ω, in units of ° C.$^{-1}$, plotted logarithmically against temperature for various relative humidities. The reason for changing round the co-ordinates between Fig. 4 and 5 is that σ is strongly dependent upon temperature, and ω upon relative humidity. Were the co-ordinates not changed round, one or other set of curves would be inconveniently steep and crowded.

c, the specific heat of the moist cotton, in cal. per degree per g. of *dry* cellulose. For lack of better information we will assume the value 0·32 cal./° C./g. given for (dry ?) cellulose in the textile section of I.C.T. to be correct for dry cotton. There exist more reliable data on the specific heat of water absorbed by cellulose in the form of bleached sulphite pulp.[6] The average value between the range of moisture regains of 2 % and 12 %, and between temperatures of 5° c. and 20° c., was 1·09 cal./° c./g. These workers do not quote a value for the cellulose. Taking, then, this mean value for the water, and assuming that the heat capacities of water and cellulose are additive, we get for the specific heat of moist cellulose per g. of *dry* cotton

$$c = 0{\cdot}32 + 1{\cdot}09\,M \text{ in cal./° c./g.} \qquad . \quad . \quad . \quad (18)$$

q, the heat given out when 1 g. water vapour is absorbed by a large quantity of cotton containing a given initial proportion of moisture. Fig. 6 shows q for scoured and bleached cotton in cal./g. of water vapour, plotted against the R.H. at which the cotton is in equilibrium when absorbing moisture, for a temperature of 25° c. The data were obtained from a paper by Rees,[7] and the values for R.H.'s from 0 % to 65 % were the result of direct experiment, whilst those for higher humidities were obtained by calculation from the absorption isotherms of Urquhart and Williams. Rees's figures were for the heat of absorption from the liquid. To these were added the latent heat of condensation of water at 25° c. It is evident that q will vary with temperature. The variation of the heat of absorption from the liquid could be calculated from the specific heats of free water and of the bound water if the absorption were reversible. To this could be added the known temperature variation in the latent heat of condensation of water. The

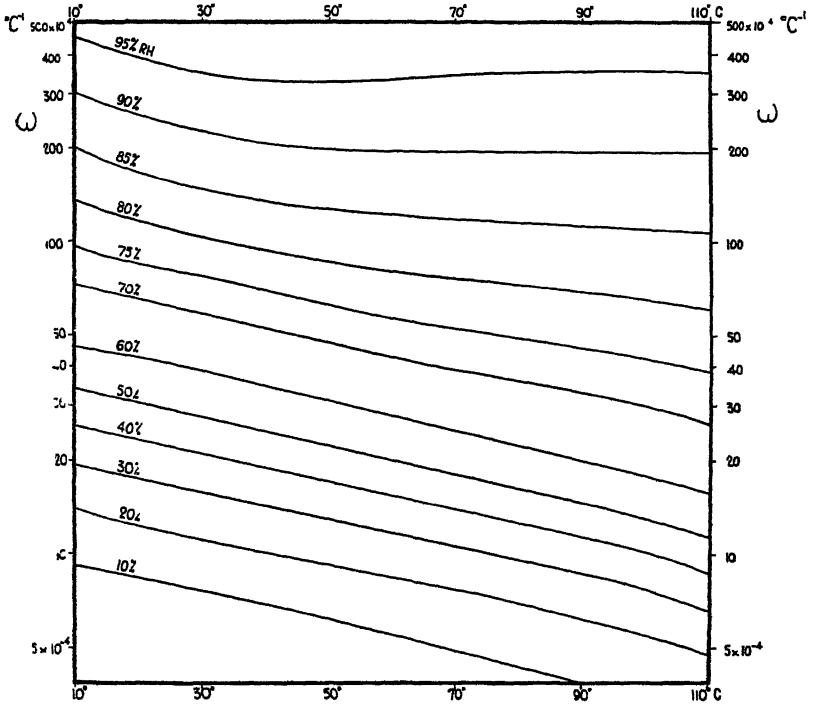

FIG. 5.—ω plotted logarithmically against temperature for various relative humidities.

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[6] Shipley, Campbell and Maass, *Can. J. Res. B*, 1939, 17, 40.

[7] Rees, *Shirley Inst. Memoirs*, 1947, 21, 333; shortly to appear in *J. Text. Inst.*

absorption process is actually far from reversible, however. An alternative method of finding the temperature effect would be to calculate the heat of absorption from Urquhart and Williams's isotherms; but this process is so inaccurate owing to uncertainty in measuring the slope of an experimental curve (see Rees, loc. cit.) that it was thought better in the absence of direct experimental data to proceed by the first method as if the absorption process were reversible. In Fig. 6 is shown dotted a curve for q at 100° C. estimated in this way.

Experimental quantities dependent upon the density of the package as well as specific properties of the cotton are as follows.

g is the ratio of the " no absorption " diffusion coefficient (D'') for water vapour in the package to the value (D^*) in free air. g is thus a measure of

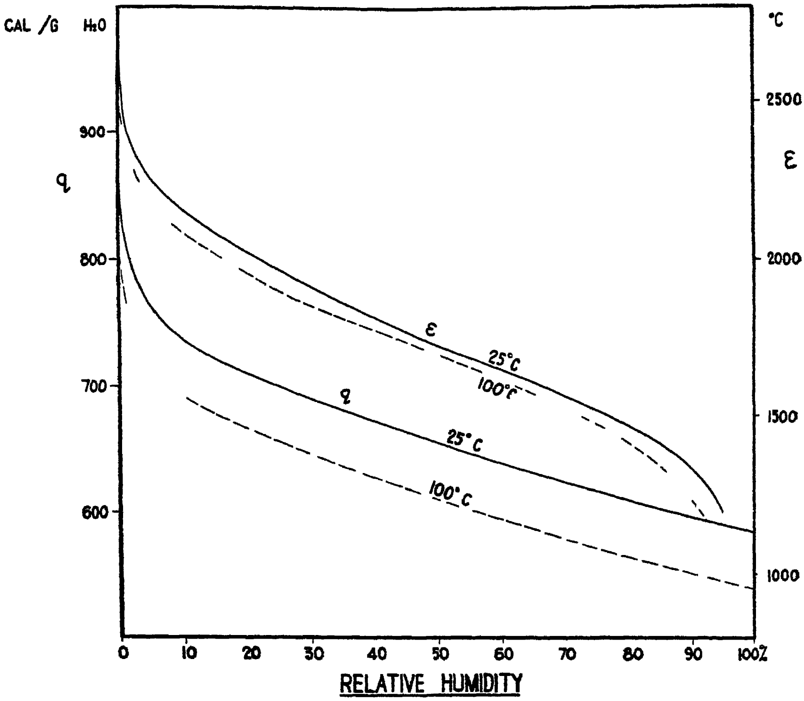

Fig 6.—q and ε plotted against relative humidity for 25° and 100° C.

the obstructive effect of the cotton hairs, and is largely a geometrical quantity, though the extent of diffusion through the hairs themselves also comes in. It can be determined by means of continuous-flow diffusion experiments, or by calculation from experiments with unsteady flow. It is not likely to be seriously affected by temperature or humidity, except in so far as these control swelling of the fibres. The data given in the author's original paper were based on comparatively few experiments on the rate of gain or loss of moisture by miniature bales of cotton. They gave values for g of 0·92, 0·46 and 0·24 at dry package densities of 0·2, 0·4 and 0·6 g./cm.^{3} respectively. These values seemed reasonable at the time on the assumption that most of the diffusion occurred through the air in the interstices. These experiments, though very relevant to the practical problem which started the work, were not very suitable for the accurate measurement of diffusion constants, and it must be reported that subsequent experiments of the same type did not confirm the original results. It is hoped that it will be possible to obtain more reliable figures from constant-flow experiments. Consequently, in the following calculations no attempt will be made to calculate absolute values for D in terms of D^*, as would be possible if g were supposed known. It will merely be assumed that g remains constant for a given package as the temperature and humidity vary, so that D'' is always proportional to D^*.

k, the thermal conductivity of loose cotton fibres compressed to different overall densities, has been determined by Speakman.[8] The cotton was conditioned to a relative humidity of 65 %, and the mean temperature during the measurement was 25° C. Fig. 7 shows a curve for k plotted against ρ. It is likely that k will increase somewhat with moisture content, but to what extent is not known.

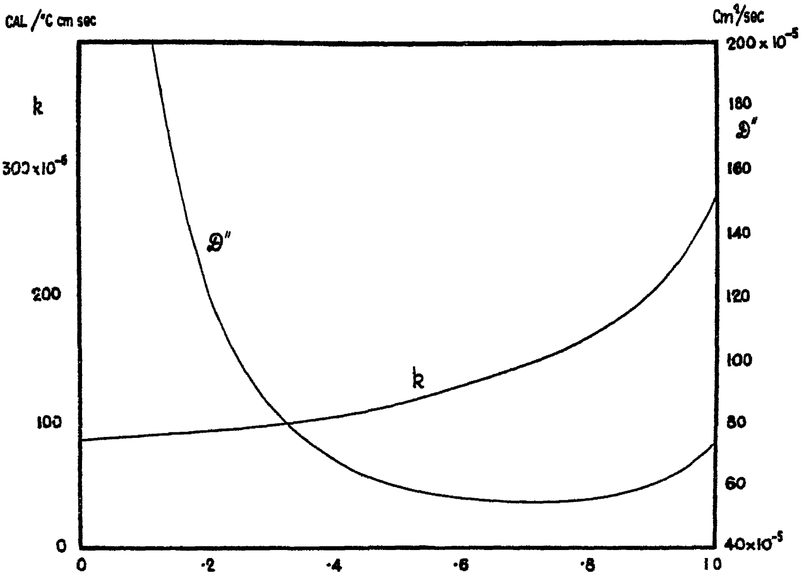

FIG. 7.—k and D' plotted against overall dry density.

Derived Quantities.—The following are quantities derived from the foregoing experimental data, which will be required in the calculation of diffusion coefficients and amplitudes.

Specific properties of the cotton, not dependent on the density of packing, are as follows.

ε is defined as q/c. It may therefore be thought of as a constant concerned with the rise in temperature produced when the material absorbs moisture. It depends upon the moisture content and the temperature much as does g. Curves showing ε against R.H. for 25° C. and 100° C. shown in Fig. 6. The unit is ° C.

$1 + \varepsilon\omega$ is the ratio of the " no absorption " to the " constant vapour concentration " coefficients of diffusion of heat through the cotton. $1/(1 + \varepsilon\omega)$ is shown plotted logarithmically against temperature for various R.H.'s in Fig. 8. It is a pure number.

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[8] Speakman, *J. Text. Inst.*, 1930, 21, T29.

λ and ν are defined as $\frac{\gamma\omega}{1+\gamma\sigma}$ and $\frac{\varepsilon\sigma}{1+\varepsilon\omega}$ respectively. Since γ is dependent upon the density of packing, λ is also, strictly speaking, so dependent. However, $\gamma\sigma$ is usually of the order of several thousand, and in this case λ can be taken as equal to ω/σ, which does not depend upon ρ. λ and ν are quantities concerned with the coupling between the diffusion processes for heat and moisture. Since they are not needed separately in order to calculate the rate of diffusion of moisture when the initial disturbance is one of relative humidity only, they are not shown plotted here. They are needed, however, in order to calculate temperature changes due to a moisture disturbance, or vice versa; and the author will be glad to supply data to anyone interested in such calculations with respect to cotton.

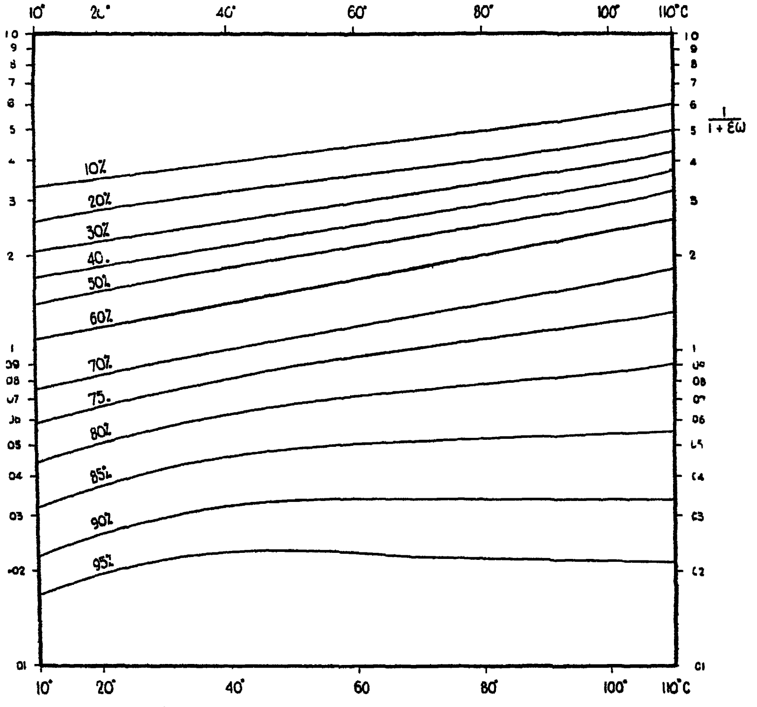

FIG. 8.—$1/(1+\varepsilon\omega)$ plotted against temperature for various relative humidities.

$\lambda\nu$, which is a pure number less than unity, may be considered as giving the strength of the coupling between the diffusion processes. Since in connection with cotton the coupling is nearly always strong, and $\lambda\nu$ is very close to unity, $(1-\lambda\nu)$ is usually a more convenient form. When, as is nearly always the case, $\gamma\sigma$ is large compared with unity, $(1-\lambda\nu)$ can be taken as equal to $1/(1+\varepsilon\omega)$. The only exception to this would be the case of a light fluffy mass of cotton fibres at a temperature in the neighbourhood of 100° C., when $\gamma\sigma$ might become comparable with unity.

γ is a derived quantity dependent upon the packing density. It is defined as $\frac{\rho\,\rho_s}{\rho_s-\rho}$ where ρ and ρ_s are the overall dry density of the package and the dry density of the cotton fibre respectively. It is the mass of solid containing unit pore space.

Calculation of Diffusion Coefficients.—The aim now is to calculate from the data given above the way in which we should expect D, $\boldsymbol{D}$ and λv to vary with the temperature and average R.H. during the diffusion process. We can then use the relations and nomograms given in the first part of this paper to determine the behaviour of the diffusion coefficients of the " normal co-ordinates " and their relative amplitudes.

We have seen that D'' is equal to gD^*, where g is a factor dependent upon the density of packing but not very much on temperature or humidity. Reference to the original paper will show that $D = D''/(1 + \gamma\sigma)$. Hence we have $D = gD^*/(1 + \gamma\sigma)$. Since unity can nearly always be neglected in comparison with $\gamma\sigma$, however, we can write this

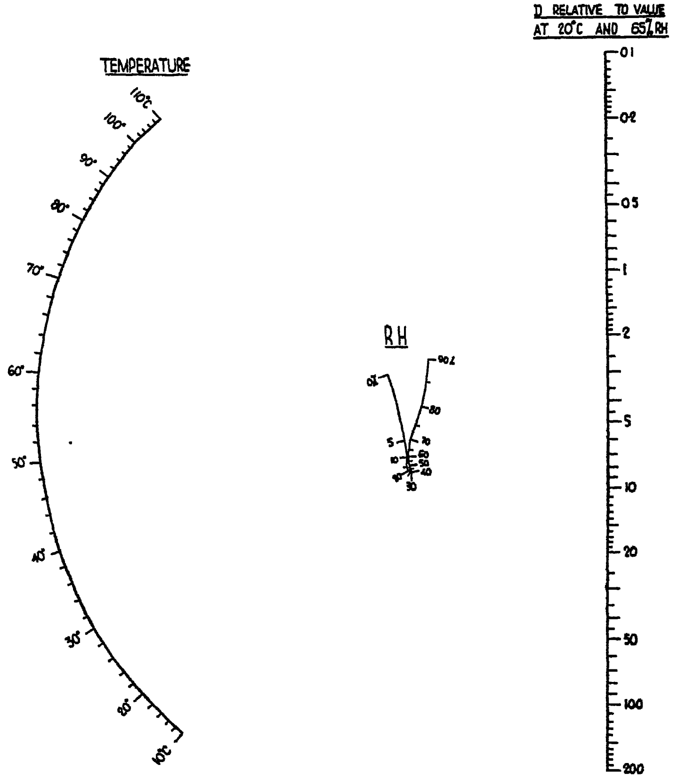

Fig. 9.—Nomogram for variation of D with temperature and relative humidity.

$$D \sim \frac{g}{\gamma} \cdot \frac{D^*}{\sigma} \quad . \quad . \quad . \quad . \quad . \quad (19)$$

where the first factor depends upon the density but not on the temperature and humidity; whilst the second factor depends only upon the latter conditions. To find how D varies with temperature and humidity, therefore, we are only concerned with D^*/σ. To facilitate calculation, this relation is shown in Fig. 9 in the form of an empirical nomogram. Since we are ignoring the factor g/γ, the units used for D are immaterial, and the D scale is constructed to give D in terms of its value at 20° C. and 65 % R.H. These conditions were chosen as lying within the standard range used for textile testing. The nomogram was originally made to agree exactly with the data for all humidities at 30° C. and 90° C. and for all temperatures at 30 % and 80 % R.H. A slight readjustment was then made at the lower end of the temperature scale to bring about more general agreement. The nomogram represents the data as closely as the limited accuracy of the latter warrants. (It must be remembered that the curves for σ were obtained by measuring the slopes of experimental curves—always an inaccurate process—followed by two-dimensional smoothing.)

In order to work out the effect of coupling, we need to know D in absolute terms, and must therefore assume a value for g. The author's experiments with miniature bales have led to apparent values for g varying over a range of 6 : 1 for a given density. This may have been due to differences in packing of the cotton, or more likely to differences in the past history of the cotton leading to variations in σ. Fortunately, for many applications it is only necessary to show that D and $\boldsymbol{D}$ are not of the same order. When more than this is required an experiment should be done under given conditions on a sample of the actual type of package concerned, when the theory can be used to predict the effects of temperature and humidity variations.

DIFFUSION COEFFICIENTS AND AMPLITUDES

	ρ = 0·2 g./cm.³			ρ = 0·5 g./cm.³		
	20 % R.H.	65 % R.H.	90 % R.H.	20 % R.H.	65 % R.H.	90 % R.H.
20°	4·5 34 4·1 130	3·1 12 2·5 140	0·93 3·2 0·72 160	1·4 16 1·3 63	0·92 5·7 0·80 66	0·28 1·5 0·24 62
50°	28 41 18 160	21 16 9·3 230	5·0 4·0 2·3 250	8·4 20 6·4 76	5·7 7·7 3·4 99	1·5 2·0 0·86 110
80°	140 49 39 420	90 20 17 690	D $\boldsymbol{D}$ D_1 D_2	41 24 17 140	27 9·8 7·4 210	
20°	0·094 0·0037	0·192 0·0040	0·22 0·0013	0·050 0·0016	0·13 0·0019	0·15 0·0006
50°	0·34 0·050	0·39 0·041	0·42 0·0010	0·25 0·027	0·38 0·023	0·39 0·0062
80°	0·21 0·20	0·17 0·11	p n	0·30 0·147	0·24 0·087	

The figures in each cell of the top half are for diffusion coefficients, the arrangement being as shown in the cell for 80° and 90 % R.H. The unit is 10^{-5} cm.²/sec.

The figures in the bottom half are the relative amplitudes of the secondary wave, as explained in the text.

For purposes of illustration, however, we will assume a value of 0·2 for g to hold over the dry density range 0·2 to 0·5 g./cm.³ At 20° C. and 65 % R.H., this would give values for D of $3{\cdot}0 \times 10^{-5}$ and $0{\cdot}9 \times 10^{-5}$ cm.²/sec. for dry densities of 0·2 and 0·5 g./cm.³ respectively.

Turning now to the thermal diffusion coefficients, we have $\boldsymbol{D}'' = k/\rho c$ and $\boldsymbol{D} = \boldsymbol{D}''/(1 + \varepsilon\omega)$. Thus $\boldsymbol{D}''$ is considerably dependent upon the density. Its dependence on temperature and humidity is not known but is likely to be moderate. Fig. 7 shows a curve for $\boldsymbol{D}''$ against ρ under the conditions of Speakman's determinations of k, viz. 25° C. and 65 % R.H. In the absence of more extensive data, we will take this curve as applying to all conditions. $\boldsymbol{D}$ can be calculated with the aid of the curves for $1 + \varepsilon\omega$ in Fig. 8.

The calculation of D_1, D_2, p and n can now be done by a straightforward application of the nomograms in Fig. 1–3, or of the expressions on which they are based. By way of illustration this has been done for loose cotton fibres compressed to overall dry densities of 0·2 and 0·5 g./cm.³ at temperatures 20°, 50° and 80° C., and R.H. of 20 %, 65 % and 90 %. The results are set forth in the table, whose arrangement should be clear from the legend. Figures have not been given for 80° C. and 90 % R.H. because under these conditions the vapour pressure would be a considerable fraction of atmospheric pressure, and fluid flow would be taking a notable part in the process.

It will be noticed how, as the temperature rises, the moisture diffusion coefficient D, which is at first much smaller than the thermal diffusion coefficient $\boldsymbol{D}$, eventually becomes much larger. It will be seen how the diffusion coefficient D_1 for the slower normal function is always less than either D or $\boldsymbol{D}$, but never by a factor of less than ½. On the other hand D_2 is always much greater than D or $\boldsymbol{D}$. The figures for n show that the secondary wave is of very small amplitude, as judged by the total moisture content, at low temperatures, but becomes appreciable at high temperatures. However, the figures for p show that when the package is subject to a thermal disturbance only, the secondary temperature wave may be of important magnitude even at room temperatures.

The author's thanks are due to the Director and Council of the British Cotton Industry Research Association for permission to publish this paper.

Summary

The paper is concerned with developing the conclusions drawn in a previous paper on the phenomena shown by two coupled diffusion processes—in this case, those of moisture and heat through a porous absorbent body such as cotton in bulk. It is shown that simplifications can be made to the equations where the coupling is very weak or very strong, where the two elementary diffusions occur at very different rates or where attention is confined to disturbances in one variable only. Nomograms are provided to simplify numerical treatment. The theory is applied to the case of compressed cotton fibres over a range of temperatures and humidities and at two values of package density.

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THE MEASUREMENT OF THE EFFECTIVE PORE SIZE AND OF THE WATER-REPELLENCY OF TIGHTLY WOVEN TEXTILES*

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In recent years considerable work has been done in attempting to develop highly water-resistant, vapour-permeable fabrics. To evaluate properly such progress as is made in this field, it is first necessary that suitable methods be available for testing and comparing the various fabrics as they are developed. To accomplish this end, it should be possible to measure quantitatively those physical properties of the fabrics which contribute to their overall effectiveness. As will be shown, the two most important properties to be measured are pore size and degree of water-repellency. This paper describes methods by which these two important properties of water-resistant, vapour-permeable fabrics can be quantitatively determined.

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Method for Measurement of Effective Pore Size

The method to be described for measurement of effective pore size is a modification of the "pressure of displacement method" which has been used extensively for the determination of the pore sizes of various types of materials.[1 2 3 4 5 6]

The porous medium (textile) to be tested is first saturated with a given liquid, and then placed in a suitable holder which permits the introduction of a thin layer of the saturant over the test-piece. Air is introduced to the holder at a point below the porous medium and the air pressure is slowly increased until the liquid is displaced from one or more pores of the sample causing air bubbles to rise through the thin layer of the liquid.

Under these conditions the following equation applies :

$$r = \frac{2\,S\,(\cos\,\theta)}{P\,g} \quad \ldots\ldots \quad (1)$$

wherein r represents the radius of the smallest pore from which liquid has been displaced, S the surface tension of the liquid, P the maximum air pressure applied, g the acceleration of gravity and θ the angle of contact formed by the liquid against the walls of the capillary pore.

In the measurement of pore radius through application of (1), a zero contact angle-forming liquid is used, because the independent determination of a finite contact angle is difficult. For a particular liquid at a given temperature the surface tension S is constant, and (1) resolves to the following :

$$r = \frac{K}{P} \quad \ldots\ldots \quad (2)$$

where $K = 2S/g$, since the saturating liquid is so chosen that $\cos\,\theta = 1$. In measuring pore sizes by this method one need know only the surface tension of the saturant used and the pressure required to force this liquid from the pores.

For the successful application of this method the liquid used must not only be a zero contact angle-forming liquid, it must also be a liquid that does not cause the fibres of the fabric to swell, thus changing the pore size, and it must be a liquid that does not dissolve any of the finishing materials or natural products from the fabric, thus changing the water-repellency. Preliminary tests indicated that certain organic liquids such as alcohols (e.g., *iso*propyl) glycols (Cellosolve) and mineral oils (Finol) were quite satisfactory from the standpoint of these three requirements.

In applying the method to textiles, it has been found satisfactory to take as the end-point the pressure reading at which air bubbles are discharged from a given number of pores, usually ten, on a circular area 2¼ in. diam. (area = 3·93 sq. in.). These ten pores are the largest pores in the area of the textile exposed to test. In testing water-repellent textiles, it is important to know *maximum* pore radii because the first failure of the cloth when exposed to water occurs as the liquid penetrates the largest pores.

Apparatus and Procedure.—An apparatus suitable for this work is illustrated in Fig. 1. A sample of the textile to be tested (about 3¼ × 5 in.) is first saturated by immersion for a period of 4 or 5 min. in a zero contact angle-forming liquid. The sample is then clamped in place in holder A. Petcock B is closed and the saturating liquid is poured over the top of the sample to a depth of from 1/16 to ⅛ in. Stopcock C is opened to admit water to the air pressure bulb E.

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[1] Bechhold, *Z. physik. Chem.*, 1908, **64**, 328 ; *Kolloid-Z.*, 1934, **66**, 329.

[2] Bigelow and Bartell, *J. Amer. Chem. Soc.*, 1909, **31**, 1194.

[3] McBain and Kistler, *Trans. Faraday Soc.*, 1930, **26**, 157.

[4] Stamm, *J. Agric. Res.*, 1929, **38**, 23.

[5] Bell, Cutter and Price, *Wetting and Detergency* (Chemical Publishing Company of N.Y., Inc., 1937), p. 19.

[6] Bartell and Carpenter, *J. Physic. Chem.*, 1923, **27**, 252 ; Bartell and Osterhof, *J. Physic. Chem.*, 1928, **32**, 1553 ; Bartell and Miller, *Ind. Eng. Chem.*, 1928, **20**, 738 ; Bartell and Smith, *Ind. Eng. Chem.*, 1929, **21**, 1102 ; Bartell and Jennings, *J. Physic. Chem.*, 1934, **38**, 495 ; Bartell and Walton, *J. Physic. Chem.*, 1934, **38**, 503 ; Bartell and Benner, *J. Physic. Chem.*, 1942, **46**, 847.

The rate of flow of water is regulated by stopcock (or needle valve) D. Stopcock G also is open permitting water to flow into the glass tube F of about ¼ in. diam, thereby establishing a hydrostatic pressure which is transmitted to the air in bulb E and holder A. A graduated scale is used to measure the hydrostatic head, i.e., the distance between the top of the water column in the bulb E and the top of the column in tube F. When the end-point is reached (i.e., when air bubbles appear from ten pores), valves G and D are closed simultaneously and the height of the water column is recorded. A zero reading is obtained by opening stopcocks G and B.

The method has been employed with different types of fabrics having maximum pore radii ranging from about 6 microns (English Shirley Cloth and American Jo Cloth) to about 100 microns (a poplin). The method has been found to be equally applicable to textiles woven from synthetic fibres and to cotton fabrics, to textiles treated with water-repellent finishes and to untreated textiles, to textiles wetted wholly or partially with water and to dry textiles.

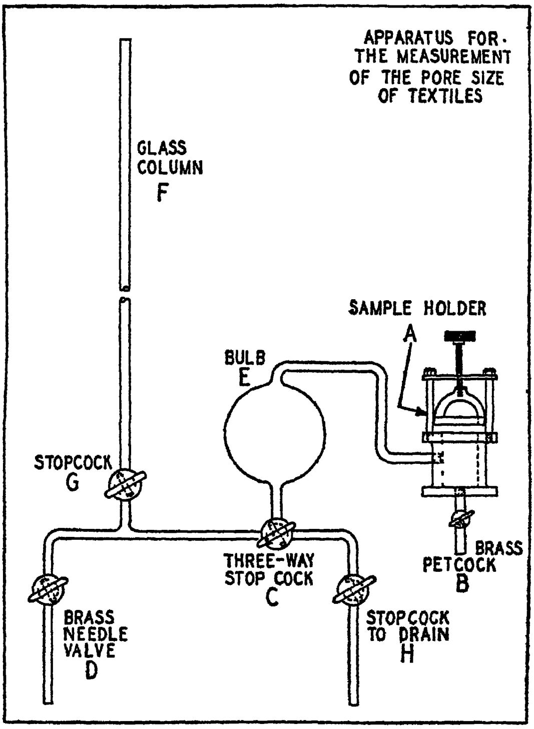

Fig. 1.

In Table I are given data obtained with ten different "water-repellent" fabrics, the effective pore radii of which were obtained both with Finol and with 95 % denatured ethyl alcohol The pore radii determined with the two liquids

TABLE I

Comparative Pore-size Measurements on Water-repellent Fabrics made with Finol and with 95 % Denatured Ethyl Alcohol as Saturating Liquids

Fabric Number	*Data obtained with Finol* $S = 28{\cdot}9$ dynes/cm.		*Data obtained with Alcohol* $S = 22{\cdot}9$ dynes/cm.	
	Air Pressure (cm. H_2O)	Pore Radii (Microns)	Air Pressure (cm. H_2O)	Pore Radii (Microns)
1	36·4	16·2	27·6	16·9
2	36·2	16·3	26·8	17·4
3	24·5	24·1	18·4	25·4
4	23·5	25·1	18·1	25·8
5	23·5	25·1	17·8	26·2
6	21·4	27·6	16·8	27·8
7	20·5	28·8	15·9	29·4
8	19·6	30·1	16·4	28·1
9	18·9	31·2	15·3	30·5
10	6·0	98·4	4·3	109·0

are seen to give reasonable agreement. The values given for Finol represent the mean of ten runs, the average % deviation thus obtained for each textile being approximately 3·1 %. The values given for alcohol represent the mean of four runs and the average % deviation was, in this case, approximately 2·2 %. All measurements were made at approximately 25° C.

Method for Measurement of Degree of Water-repellency

In this work an attempt has been made to define quantitatively the term "water-repellency" according to fundamental concepts of the wetting of porous solids by liquids, and furthermore to establish a method whereby the degree of water-repellency of fabrics, as so defined, can be measured.

Water-repellency may be defined in terms of the angle of contact of solid and liquid or, perhaps more advantageously, in terms of the cosine of that angle. A water-repellent material is one which exhibits a contact angle with water of greater than 90° ($\cos\theta < 0$). Maximum water-repellency would be evidenced if the angle of contact were 180° ($\cos\theta = -1$). As a measure of water-repellency then, one may use the numerical scale of $\cos\theta$ from 0 to -1. The value of ($-\cos\theta$) for a particular material may be multiplied by 100 to indicate the percentage of the theoretical maximum water-repellency exhibited.

Behaviour of Water in Capillaries.—The behaviour of water in capillaries can be predicted from the pressure-of-displacement equation (1) as follows. Water will tend spontaneously to advance into a capillary, the surface of which is composed of a material on which water forms an advancing contact angle of less than 90°. An opposing pressure is required to prevent the advance of water into this capillary and the smaller the angle of contact of the water on the capillary wall, the greater will be the pressure required. If the advancing contact angle of water against the wall of the capillary is greater than 90°, then pressure must be applied to force water into the capillary. The greater the angle of contact, the greater will be the pressure which must be applied. If, when water is receding from a capillary, the receding angle is less than 90°, pressure will be required to force the water from the capillary; however, water will tend spontaneously to recede from the capillary if the receding contact angle is greater than 90°.

It is obvious from the foregoing that if the pores of a water-repellent fabric ($\cos\theta < 0$) are within the capillary range (i.e., the pressure-of-displacement equation applies), then the fabric will also be water-resistant, for pressure must be applied to force the water into and through the pores of the fabric. For a fabric of given pore size, the water-resistance will increase as the water-repellency approaches a value of -1. Likewise, for a given water-repellent surface, the water-resistance increases as the pore size decreases.

Water-resistance against Water-repellency.—It is of importance to distinguish clearly between the terms *water-resistance* and *water-repellency*. Water-resistance is determined not only by the degree of water-repellency but also by the effective pore radius. To obtain a fabric of high water-resistance, there must exist not only a high degree of water-repellency but also the pore radii must be small.

In this research, methods have been established whereby the contact angles of water on repellent fabrics may be measured, and, in accordance with the definitions set forth above, the cosines of these angles are used as a measure of the degrees of water-repellency of the fabrics. Information thus obtained, together with pore-size measurements made in the manner just described, permits a separation of the two variables contributing to the water-resistance of repellent textiles. This feature distinguishes the test-methods here reported from those previously used which were, for the most part, directed merely toward the evaluation of water-resistance.

Factors Affecting Water-repellency Measurements.—The determination of water-repellency by contact angle measurements is complicated by the existence of two stable solid-water-air contact angles (an advancing contact angle and a receding contact angle) and also by the effect of surface roughness.

The advancing angle is the characteristic angle formed when a liquid is caused to advance over a solid surface or into capillary pores, whereas the receding contact angle is the characteristic angle formed when the same liquid is caused to recede from the solid surface or capillary pores. In the testing of water-repellent fabrics it is necessary to evaluate the advancing angle in order to determine the resistance of the fabric to penetration by water, whereas it is necessary to evaluate the receding angle in order to determine the ease with which a fabric will shed water. The receding angle is, in effect, a measure of the water-shedding properties of a fabric, such shedding occurring readily only when the receding angle is greater than 90°.

The measurement of both the advancing and receding contact angles of water on fabrics is complicated by the surface roughness of the fabric.[7] It is a well-known fact that the advancing contact angle of water against a water-repellent solid having a microscopically plane surface is lower than the advancing angle formed against the identical solid possessing a somewhat roughened surface. The effect of the roughness phenomenon in increasing the effective advancing contact angle is relatively great for good water-repellent cotton fabrics (on which the advancing angle is apparently increased from about 110° to 140° or 150°), but is rather small for water-repellent Nylon and Vinyon fabrics (on which the advancing angle is apparently raised only from about 110° to 120°). Cotton fibres are exceedingly discontinuous and cotton textiles are covered with an outer layer of fine fuzz (ends of fibres). Nylon, Vinyon, and most other synthetic fibres, on the other hand, are relatively round and smooth. These characteristics may account for the fact that it is possible to produce water-repellent cotton fabrics which are more effective than water-repellent synthetic fibre fabrics.

In the work here reported, only advancing contact angles (i.e., the angle of importance to the property of water-resistance) have been measured. No attempt has been made to determine quantitatively the degree of roughness of fabrics although all data given below are for cotton fabrics wherein the roughness effect was considered to be about equal for all fabrics.

Procedure for Measurement of Water-repellency.—Modification of the pressure-of-displacement method above described provided a satisfactory method for measuring the angle of contact of water against repellent fabrics, and thus made possible the determination of the degree of water-repellency as measured on the convenient and significant cos θ scale.

From (1) and (2)

$$\cos\theta = \frac{Pr}{K}, \text{ where } K = \frac{S2}{g} \quad . \quad . \quad . \quad . \quad (3)$$

Since, in this instance, the significant angle is the advancing contact angle, (θ^A_W), of the water against the fabric, the equation may be written :

$$\cos\theta^A_W = \frac{P_W r}{K_W} \text{ (for water } K_W = 0{\cdot}167) \quad . \quad . \quad . \quad (4)$$

The value of cos θ^A_W represents the degree of water-repellency of a fabric and can be obtained by determining r, the effective pore radius of the textile (obtained by the method described in the section on pore radius), and P_W, the minimum pressure required to force water into and through pores of radius r.

The pressure, P_W, is the water-resistance of the fabric and is determined with apparatus similar to that described by Slowinske[8] for measuring water-resistance. The end-point is taken to be that pressure at which water droplets appear at ten different points on the upper side of the fabric. (Compare with the end-point for the pore-size determination.) The area of the fabric exposed to this test is the same (3·93 sq. in.) as that for the pore-size determination. The rate of pressure increase should not exceed 4 in. hydrostatic head increase per minute and as the end-point is approached a somewhat lower rate is desirable.

The measurement of r, the effective pore radius of the fabric, is accomplished by measuring the pressure necessary to cause an organic liquid (which forms a zero contact angle with the fabric) to recede from the pores of the textile. If (2) is modified to indicate the use of an organic liquid which forms a zero receding contact angle ($\cos\theta_o^R = 0$), one has:

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[7] Wenzel, *Ind. Eng. Chem.*, 1936, **28**, 988.

[8] Slowinske, *Amer. Dyestuff Rep.*, **30**, No. 1, *Proc. Amer. Assoc. Text. Chem. Col.*, 1941, 6.

$$r = \frac{K_o}{P_o} \qquad (5)$$

In determining the value of $\cos\theta_w^A$ (or the degree of water-repellency) of a treated fabric, it is not necessary to make the intermediate calculation of r since a combination of (4) and (5) shows that:

$$\cos\theta_w^A = \frac{P_w K_o}{P_o K_w} = \frac{K' P_w}{P_o} \qquad (6)$$

where

$$K' = \frac{K_o}{K_w} = \frac{S_o}{S_w}$$

Water-repellency of Different Fabrics with given "Water-repellent" Treatments.—To test the reliability of the above-proposed method for determining the degree of water-repellency of textiles, two sets of five fabrics each were obtained for study. Within each set, the five fabrics were all of different weave but each had been treated with the same commercial "water-repellent" material (Group A had all been given a Zelan treatment and Group B a Ponlitex treatment).

It would be expected that the values of $\cos\theta_w^A$ would be identical for a given water-repellent treatment regardless of the type of fabric to which it was applied, provided the coverage was uniform in all cases, and that there were no great variations in surface roughness. The results obtained are given in Table II. Each value is an average of values obtained on at least ten different samples of each fabric.

TABLE II

WATER-REPELLENCY OF DIFFERENT FABRICS WITH TWO TYPES OF COMMERCIAL WATER-REPELLENT TREATMENTS

Group	Fabric	P_w (cm. of Water Head)	P_o (cm. of Water Head)	Water-repellency ($-\cos\theta_w^A$)
Type A (Zelan treated)	1	41·6	28·0	0·60
	2	47·6	27·9	0·69
	3	49·3	28·6	0·69
	4	63·4	38·3	0·67
	5	74·2	47·9	0·62
			Average	= 0·65
Type B (Ponlitex treated)	6	11·5	6·0	0·77
	7	40·1	21·4	0·75
	8	43·6	24·5	0·72
	9	65·9	36·3	0·73
	10	68·9	36·4	0·76
			Average	= 0·75

NOTE.—Finol used as the zero contact angle-forming liquid.

$K^1 = K_o/K_w = S_o/S_w = 28{\cdot}9/72{\cdot}0 = 0{\cdot}402$

$\text{Cos}\,\theta_w^A = 0{\cdot}402\,\frac{P_w}{P_o}$

The fairly close agreement in the values for $\cos\theta_w^A$ within each of the two groups as shown in Table II indicates that the actual water-repellency of different fabrics treated with the same water-repellent treatment is practically the same. The agreement among the $\cos\theta_w^A$ values of the fabric in Group B is somewhat better than that for Group A, and it should be mentioned that while the five fabrics in Group B were especially treated with Ponlitex for these tests the fabrics in Group A were obtained from several different commercial sources and may therefore not have had exactly the same treatment. To obtain extremely good agreement among values of $\cos \theta^A_W$ for different fabrics treated with the same water-repellent, it would be necessary not only to make sure that the treatments were identical, but also to take special precautions against contamination of the treated fabric surfaces since hydrophobic surfaces possessing high degrees of water-repellency may become slightly altered through handling or by adsorption of foreign substances. Considering the experimental difficulties involved in obtaining uncontaminated and reproducible surfaces, the agreement shown in Table II is considered good and lends support to the use of the pressure-of-displacement method as a means for measuring the degree of water-repellency of treated fabrics.

It is interesting to note that the five fabrics within each of the two groups, A and B, exhibit quite different values of water-resistance (varying from 42 to 74 cm. of water head for Group A and from 12 to 69 cm. of water head for Group B), this difference being due to the difference in pore size existing among the various fabrics of each group. If the fabrics within each group had possessed the same pore size they would have exhibited practically the same water-resistance.

Water-repellency of a Given Fabric with Different Water-repellent Treatments.—Many different water-repellent treatments on various types of fabrics have been tested for water-repellency by this pressure of displacement method. Table III gives representative data for eight different water-repellent treatments which had all been applied to different samples of the same grey goods. The values shown are averages of at least ten runs on each fabric. The zero contact angle-forming liquid used was Finol.

TABLE III

WATER-REPELLENCY OF A GIVEN FABRIC WITH DIFFERENT WATER-REPELLENT TREATMENTS

Treatment Number	P_W (cm. of Water Head)	P_0 (cm. of Water Head)	Water-repellency ($-\cos \theta^A_W$)
1–A	30·9	20·6	0·60
2–A	38·5	20·8	0·74
3–A	30·2	19·6	0·62
4–A	31·1	18·6	0·66
5–A	31·7	20·7	0·61
6–A	31·3	22·8	0·55
7–A	30·9	20·5	0·61
8–A	39·5	23·5	0·67

TABLE IV

CALCULATED WATER-RESISTANCE BASED UPON A UNIFORM PORE SIZE

Treatment Number	Water-resistance Based on the Pore Size of Fabric 8–A (cm. of Water Head)	Water-resistance actually Exhibited (cm. of Water Head)
1–A	35·2	30·9
2–A	43·5	38·5
3–A	36·2	30·2
4–A	38·6	31·1
5–A	36·0	31·7
6–A	32·3	31·3
7–A	35·4	30·9
8–A	39·5	39·5

The values of water-repellency for the eight treatments as measured by cos θ_w^A are shown in the last column of Table III. It is interesting to note that the fabric with the highest water-repellency (No. 2–A) did not exhibit the highest water-resistance (P_w value), nor did the fabric with the lowest water-repellency (No. 6-A) possess the lowest water-resistance. This was due in part to variations in pore size brought about by differences in the extent to which the various treatments tended to fill the pores of the goods to which they were applied. The data shown in Table IV give the hydrostatic pressures which it may be assumed the fabrics would have resisted had they all possessed the same pore size. The calculations are based on the smallest pore radius exhibited by any of the fabrics in Table III, namely, that of fabric 8-A.

The data of Table IV are presented to emphasise again the dependency of water-resistance on pore size as well as on water-repellency. Water-resistance can be used as a measure of water-repellency only in the very specialised case (rarely, if ever, realised in practice) in which the fabrics to be compared all have exactly the same pore size.

Discussion

Of the many water-repellent finishes that have been tested during the course of this research it has been found that the best have cos θ_w^A values ranging from $-0{\cdot}6$ to $-0{\cdot}8$. It should be emphasised, however, that these values are for the material in the dry state as received from the finishing mills. It is known that the repellency of a water-repellent finish is altered to a greater or lesser degree when a treated fabric is exposed to water, dry-cleaned, washed, etc. The choice of the best finish then depends not only on the original degree of repellency of that finish but also on the extent to which it is altered under service conditions. In general, the best water-resistant fabrics will, therefore, be those made by applying the best and most durable water-repellent finishes to the most tightly woven grey goods available. The tests here described provide means by which these two contributing factors (i.e., degree of water-repellency and pore size) may be determined quantitatively.

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THE PASSAGE OF WATER THROUGH THE CAPILLARY STRUCTURE OF WOOD

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The passage of water through wood is a highly complex phenomenon.[1] This fact was appreciated at least 20 years ago by Martley[2] and Stillwell,[3] who showed that even below the fibre-saturation point the water movement under a vapour-pressure gradient is not a simple vapour-diffusion phenomenon, as had previously been supposed. They showed that calculated diffusion constants increased with an increase in moisture content. Some research workers have attempted to explain this fact on the basis of the swelling of the wood. Swelling alone cannot explain the fact. The fibre cavities, or lumina, that constitute the major void volume of all coniferous species, change but slightly in dimensions when wood shrinks and swells.[4 5] The pit-membrane pores, which are the major means of passage of vapours between adjacent fibre cavities, have been actually shown to decrease in size as the wood swells.[6] It is thus apparent that swelling alone would have the reverse effect upon the diffusion constant from that actually found.

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[1] Bateman, Hohf and Stamm, *Ind. Eng. Chem.*, 1939, 31, 1150.
[2] Martley, *Dept. Sci. Ind. Res.* (*Brit.*), Tech. Paper No. 2 (1926).
[3] Stillwell, *Dept. Sci. Ind. Res.* (*Brit.*), Tech. Paper No. 1 (1926).

Transverse-drying-diffusion constants for wood have been calculated by assuming that simple diffusion takes place independently of moisture content, using Fourier analysis methods.[7] Kollmann,[8 9] Sherwood[10] and Sherwood and Comings[11] used rate-of-drying data, and Tuttle[12] used moisture-distribution data for making calculations.[13 14] In each case, the surface moisture content was that obtained in normal wood-drying practice, 6 to 10 %. All of these investigators obtained diffusion constants consistent with theory, which has made it appear that moisture-content variations do not significantly affect the diffusion constant.

Diffusion in Water-saturated Wood

The author felt that the discrepancies between the findings of the investigators using the Fourier analysis methods and those of Martley and Stillwell might be accounted for on the basis that part of the moisture movement is due to diffusion of liquid water through the wood substance under a moisture-content gradient. It would be very difficult to differentiate experimentally between vapour diffusion and bound-water diffusion when they occur simultaneously. It was therefore decided at the U.S. Forest Products Laboratory to attempt to calculate theoretical diffusion constants from known capillary-structure data,[15] and a few reasonable assumptions, to see how these values agreed with the experimental findings.[14]

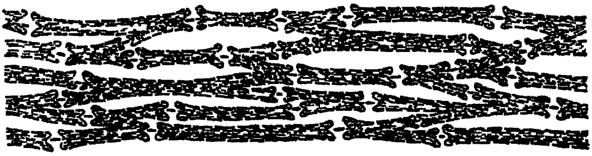

FIG. 1.—Diagrammatic sketch of a swollen tangential section of a softwood.

The first assumption, which has recently been shown by experiment to be correct, is that diffusion through the complex capillary structure of wood is analogous to the conduction of an electric current through the same capillary structure.[16] The diffusion through capillaries in parallel is additive and the resistance to diffusion through capillaries in series is additive, or the diffusion through capillaries in series is the reciprocal of the sum of the reciprocals of the diffusion through each capillary. To simplify the calculations, the analysis was confined to coniferous woods free from resin ducts. The effect of diffusion through the ray cells was neglected. Except in pines that contain horizontal

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[4] Stamm, *Ind. Eng. Chem.*, 1935, **27**, 401.

[5] Stamm and Loughborough, *Amer. Soc. Mech. Eng. Trans.*, 1942, **64**, 379.

[6] Stamm, *Physics*, 1935, **6**, 334.

[7] Ingersoll and Zobel, *Mathematical Theory of Heat Conduction* (Ginn & Co., Boston, 1913).

[8] Kollmann, *Forsch. Gebiete Ingenieurw*, 1935, **6**, 169.

[9] Kollmann, *Forsch. Gebiete Ingenieurw*, 1936, **7**, 113.

[10] Sherwood, *Ind. Eng. Chem.*, 1929, **21**, 12.

[11] Sherwood and Comings, *Vsessayuznovo Teplotechnisches Kovo Inst.*, No. 8, August (1935).

[12] Tuttle, *J. Franklin Inst.*, 1925, **200**, 609.

[13] Newman, *Cooper Union Bull., Eng. Sci.*, Ser. 5 (1932).

[14] Stamm, *U.S. Dept. Agric. Tech. Bull.*, 929 (1946).

[15] Stamm, *J. Agric. Res.*, 1929, **38**, 23.

[16] Burr and Stamm, *J. Physic. Chem.*, 1947, **51**, 240.

resin ducts, this simplification has been shown to have but a minor effect upon the results.[14] The passage of materials through coniferous woods would thus have to be through the fibre cavities in series with the pit systems and the transient cell-wall capillaries that are in parallel (see Fig. 1). A continuous passage through transient cell-wall capillaries would be in parallel with the foregoing combined path. The pit system is made up of pit chambers in series with openings in the pit membrane that comprise both larger permanent openings and openings of the transient type, as in the cell wall, that exist only when the wall is swollen. These will be called transient capillaries to emphasise the fact that they do not exist under all conditions.

The capillary data needed for calculating the diffusion through this complex system are the total fractional cross-section of all the capillaries of each type that are combined in parallel, the average length of each type of capillary, and the number of each type that are connected in series per unit distance through the wood. Good, to reasonably good, data are available for the dimensions of all of the different types of capillaries, except for the fractional transient cell-wall capillary cross-section and the total of the pit-membrane-pore capillaries.[14] The dimensions for the fractional cell-wall capillaries have been estimated by a method considered sounder than those previously used for estimating the effective capillary cross-section of membranes.[14] The pit-membrane-pore cross-section is the most variable of the capillary properties used in the calculations, as indicated by the limited data available.[11] Fortunately, rather large variations in the values used have a minor effect upon the calculations

The simple case where only one type of movement can take place, namely, that of a molecule similar to the water molecule diffusing through water-saturated wood under a concentration gradient, was considered first. For diffusion in the fibre direction [14]

$$D_l = 1/R_l = \cfrac{1}{R_a + \cfrac{1}{\cfrac{1}{\cfrac{1}{1/R_b + 1/R_c} + R_d} + 1/R_e}} + 1/R_f \quad . \quad (1)$$

where:

D_l = longitudinal-diffusion constant relative to the dimensions of the swollen wood.
R_l = total resistance of the network in the longitudinal direction per cm. cube.
R_a = resistance of the fibre cavities.
R_b = resistance of the permanent pit-membrane pores.
R_c = resistance of the transient pit-membrane capillaries.
R_d = resistance of the pit chambers.
R_e = resistance of the cell-wall capillaries to passage from one fibre cavity to the next.
R_f = resistance of the capillaries of the cell wall to continuous passage through them.

The resistance terms each include D_0 in the denominator, where D_0 is the diffusion constant for the bulk liquid. Substitution of typical values for the heartwood of a coniferous wood with a specific gravity of 0·365 gives $D_l = 0{\cdot}651\, D_0$.

A similar equation for transverse diffusion (diffusion at right-angles to the fibre direction) gives $D_t = 0{\cdot}0466\, D_0$ for the same wood. The ratio of longitudinal to transverse diffusion is thus

$$\frac{D_e}{D_t} = 14{\cdot}1$$

Fig. 2 gives the calculated values of $\frac{D_l}{D_0}$, $\frac{D_t}{D_0}$, and $\frac{D_l}{D_t}$ for the heartwood of conifers over the normal specific-gravity range of the wood. The contribution of the continuous path through the cell wall to diffusion in the longitudinal direction is negligible. The resistance of the fibre cavities to diffusion is great compared to that of the pit structures and of the cell-wall capillaries. Longitudinal diffusion, then, is limited by the void cross-section of the fibre cavities, and since this is inversely proportional to the specific gravity of the wood, the plot of D_l/D_0 against specific gravity is nearly a straight line. In the transverse direction, the contribution of the continuous path through the cell wall to diffusion is about 3 % of the total. The pit resistance is approximately twice that of the cell-wall capillaries, and their combined resistance is much greater than that of the fibre cavities. D_t/D_0 falls rather sharply with increasing specific gravity in the low-specific-gravity region, but a roughly linear relationship exists between that ratio and specific gravities higher than about 0·3. In consequence, the ratio D_l/D_t is fairly constant in the range of specific gravities normal for coniferous woods. While D_t will depend to a certain extent upon factors that are independent of the specific gravity, variations in these quantities among the common coniferous species appear to be small or to have a minor effect upon the results.

These calculated diffusion constants have been shown to agree quite well with diffusion data [16 17] and with electrical-conductivity data [18] when a correction for the taper of the fibre cavities is made in the case of longitudinal diffusion. [14 16] This agreement indicates that the estimated effective capillary cross-section of cell walls must be approximately correct.

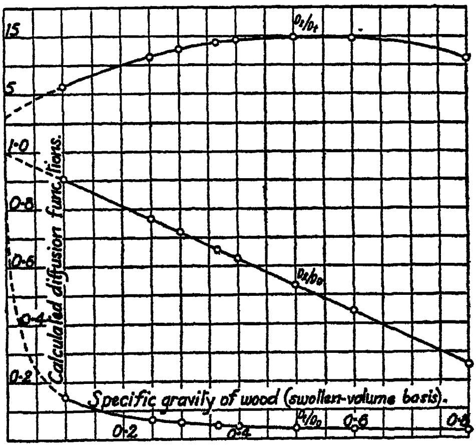

FIG. 2.—Calculated diffusion functions relative to bulk diffusion for the passage of solutes with molecules the size of the water molecule through water-saturated wood of different specific gravities.

Diffusion under Drying Conditions

The next step was to apply the foregoing methods of calculating the diffusion constants to the drying of wood that was initially below the fibre-saturation point. These calculations are more complicated for two reasons: (*a*) the dimensions of part of the capillary structure vary with moisture content, thus making it necessary to use different capillary-constant values for each lamina at right-angles to the drying gradient having an approximately constant moisture content, and (*b*) two kinds of diffusion are taking place simultaneously, a bound-water diffusion through the cell walls under a moisture-content gradient and a vapour diffusion through the coarser capillary structure under a vapour-pressure gradient. Moisture content and vapour pressure are related by a complicated sigmoid relationship. It is thus necessary to calculate the diffusion constant for a number of lamina in series, each with a different uniform moisture content, and to convert the two kinds of diffusion to a common basis.

Moisture gradients in wood are normally expressed in terms of change in weight of water per unit weight of dry wood per unit distance. In the case of diffusion, the gradient is normally expressed in terms of change in weight per unit volume per unit distance. The diffusion of both water vapour and bound water were therefore transposed to the unit-volume basis.

The diffusion of water vapour in air d_v is dependent upon the absolute temperature T and the total pressure P_a, expressed in mm. Hg, as follows.[19]

$$d_v = 0{\cdot}220 \left(\frac{T}{273}\right)^{1{\cdot}75} \cdot \frac{760}{P_a} \qquad . \quad . \quad . \quad . \quad (2)$$

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[17] Cady and Williams, *J. Physic. Chem.*, 1935, **39**, 87.

[18] Stamm, *J. Physic. Chem.*, 1932, **36**, 312.

[19] *Inter. Crit. Tables.*

This diffusion constant, in sq. cm./sec., can be transformed to a basis in which the gradient is expressed in terms of the change in relative vapour pressure, by multiplying the values by the number of g. H_2O/cc. saturated water vapour. The diffusion is then in C.G.S. units. When this is, in turn, multiplied by the rate of change of relative vapour pressure with changes in moisture content, obtained from the slope of the moisture content-relative vapour-pressure curves for wood at the moisture content and temperature under consideration, the diffusion constant is then in terms of the moisture content per unit weight of dry wood.[14] To put it in terms of the volume of swollen wood rather than weight of dry wood and in cm.²/sec., the diffusion value is finally divided by the specific gravity of the wood at test (dry weight divided by swollen volume).

In order to calculate the diffusion of bound water, it is necessary to assume that diffusion of mobile water held in polymolecular layers diffuses through immobilised water held as a monomolecular layer in the fine transient-capillary structure of the cell walls.[14] On the basis of this assumption, the bound-water diffusion d_w can be calculated by use of Einstein's diffusion equation in cm.²/sec., as follows:

$$d_w = \frac{RT}{N}\left(\frac{1}{6\pi\eta r_0}\right) \quad . \quad . \quad . \quad . \quad (3)$$

in which R is the gas constant ($8{\cdot}316 \times 10^7$), T is the absolute temperature, N is Avogadro's constant ($6{\cdot}06 \times 10^{23}$), η is the viscosity of the diffusing medium, in this case water, and r_0 is the effective radius of the diffusing water molecule. Undoubtedly, the viscosity of the surface-bound water is somewhat greater than that of normally free water, but as no data are available for the bound water the value for free water is used in the calculations. Various data indicate that about 6 % water is held by wood in a monomolecular layer.[20] On this basis, bound-water diffusion will not occur below this moisture content.

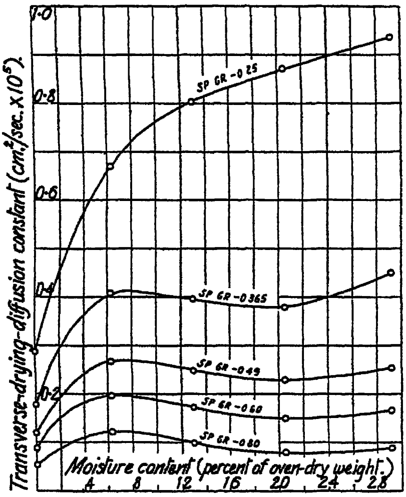

FIG. 3.—Transverse-drying-diffusion constants relative to unit dimensions of the wood, for wood with different swollen-volume specific gravities and moisture contents dried at 40° C.

To put this bound-water diffusion in the same units as the water-vapour diffusion, it is multiplied by the rate by which the volume of water per unit volume of swollen wood substance changes with the weight of moisture per unit weight of dry wood,[14] which rate is obtained from the slope of the relationship between these two quantities at the moisture content under consideration. The product in turn is multiplied by the specific gravity of the absorbed water at the moisture content under consideration [21] [22] to put the diffusion in terms of weight of water change per unit volume of swollen wood substance. The result is divided by the fractional liquid volume of the swollen cell wall to put it in terms of the liquid volume rather than the cell-wall volume and, finally, is divided by the specific gravity of the wood at test to bring the bound-water diffusion back to units of cm.²/sec.

Equations similar to (1) can be set up for lamina of different moisture content by multiplying the capillary-dimension functions by the appropriate diffusion constant corrected to identical units, that is, by multiplying the capillary-dimension functions for passage of water vapour through the microscopically visible capillary structure, by the corrected value of d_v, and by multiplying the value for the capillary function representing the passage of bound water through the cell walls by the corrected value of d_w.

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[20] Stamm and Hansen, *J. Physic. Chem.*, 1938, **42**, 209.

[21] Stamm, *Ind. Eng. Chem.*, 1938, **30**, 1280.

[22] Stamm and Hansen, *J. Physic. Chem.*, 1937, **41**, 1007.
Stamm, in *Chemistry of Wood*, by L. E. Wise (Reinhold Pub. Corp., New York, 1944).

Fig. 3 gives data for the calculated transverse-diffusion constant, at five different moisture contents, for the heartwood of coniferous woods, with five different swollen-volume specific gravities, dried at 40° c. The data show that the diffusion constant varies but slightly for woods with normal specific gravities at moisture contents higher than 6 %. The variation in the case of wood with a specific gravity of 0·25, which is lower than that of most woods, is somewhat greater. This is due to the facts that a greater proportion of the diffusion is vapour diffusion in the case of low- in contrast to high-specific-gravity woods, and that vapour diffusion is proportional to the vapour-pressure gradient rather than to the moisture-content gradient, in terms of which the diffusion is expressed.[14] The drop in diffusion constant below [illegible] fact that bound-water diffusion is no longer effective. The average diffusion constant effective for diffusion from the fibre-saturation point to any surface-boundary condition can be obtained from the areas under the curves of Fig. 3 up to the boundary condition under consideration.[14] These values vary considerably less with variations in the boundary-moisture content than the values plotted in Fig. 3. It is thus not surprising that Kollmann, Sherwood and Tuttle obtained diffusion constants that apparently are independent of the boundary-moisture-content condition. Fig. 4, 5 and 6 give the average calculated transverse-drying-diffusion constants, for wood with different swollen-volume specific gravities, for drying at several different temperatures to a surface-moisture content of 10 % in both C.G.S. and English units, together with various values calculated from drying data taken from the literature.* [2 8 9 11 14 16 17]

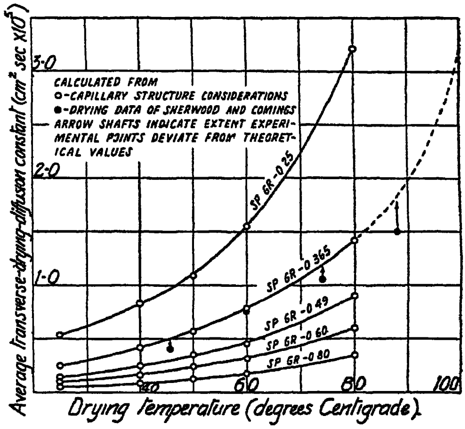

FIG. 4.—Average transverse-drying-diffusion constants relative to unit dimensions of the wood, for wood with different swollen-volume specific gravities dried at different temperatures, under relative vapour-pressure conditions that give a surface moisture content of 10 %.

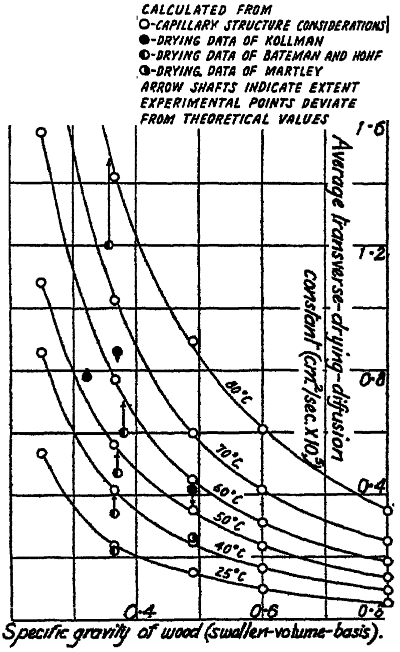

FIG. 5.—Average transverse-drying-diffusion constants relative to unit dimensions of the wood, for wood with different swollen-volume specific gravities dried at different temperatures under relative vapour-pressure conditions which give a surface moisture content of 10%.

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* Typewritten report of W. K. Loughborough and E. C. Peck, U.S. Forest Products Laboratory, Madison, Wis.

The agreement between the values calculated from capillary-structural considerations and from drying data is surprisingly good. The curves show a considerable increase in the diffusion constant with increases in temperature, with the increase being greater for the low- than the high-specific-gravity woods. This difference is due to the fact that vapour diffusion, which predominates in the case of low-specific-gravity woods, is affected more by temperature changes than is bound-water diffusion.

It is also possible to calculate the effect of drying under reduced pressure.[14] A vacuum aids only in the diffusion of water vapour at the lower moisture contents. The average effective diffusion constant at 60 mm. Hg pressure may be three to five times that at 760 mm. at 40° c. (see Fig. 7). At higher temperatures, the total pressure cannot be so low because of the greater vapour pressure of water. Because of this limitation, little is gained in increased rate of diffusion other than that due to the temperature rise alone. This fact, combined with the fact that it is difficult to heat wood under a vacuum, indicates the impracticability of drying sizeable pieces of wood under a vacuum.

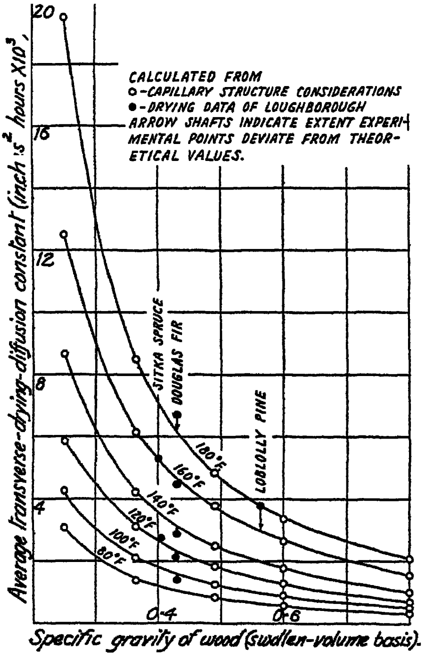

FIG. 6.—Average transverse-drying-diffusion constants relative to unit dimensions of the wood in English units, for wood with different swollen-volume specific gravities dried at different temperatures under relative vapour-pressure conditions which give a surface moisture content of 10 %.

Movement of Free Water

In considering the movement of free water in wood, the simplest case of the movement of water through completely water-saturated wood under conditions such that air-liquid menisci cannot be formed within the capillary structure will be considered first. In this case, Poiseuille's relationship for the flow of a liquid through capillary tubes should apply; in which case, the flow through a single tube will vary directly as the fourth power of its radius and inversely as its length.[14 15] For a number of tubes of equal radius and of equal length connected in parallel, the flow will vary as the number of tubes times the fourth power of the radius divided by the common length, or as the combined capillary cross-section times the square of the radius divided by the length. When two capillaries, one of which has a radius 10 times the other, are connected in parallel, the flow through the larger tube will be 10,000 times that through the smaller tube. When the two capillaries are connected in series, the flow through the two tubes will be the same. The pressure drop through the smaller tube will, however, be 10,000 times that through the larger tube. Considering the flow of water under pressure through the fibre cavities in series with the flow through the pit structure and the cell walls connected in parallel, the following reduced equation has been obtained for flow in the fibre direction through the heartwood of average conifers.[14]

$$53{,}000\, P_f = (3{\cdot}0 + 0{\cdot}0007)\, P_m \quad . \quad . \quad . \quad (4)$$

$$P_f = 5{\cdot}7 \times 10^{-5}\, P_m \quad . \quad . \quad . \quad . \quad (5)$$

where P_f is the pressure drop through the fibre cavities and P_m is the pressure drop through the pit system and cell walls. The term on the left side of (4) is for the fibre cavities. The first term in parentheses on the right side of the equation is for the pit system, and the last term is for the cell walls. About 99·98 % of the flow is through the pits. For all practical purposes, the flow through the cell wall can be neglected. The pressure drop through the fibre cavities is negligible in comparison to that through the pit system. Flow of water through wood in the fibre direction under pressure is thus almost entirely dependent upon the effectiveness of the pit capillaries.

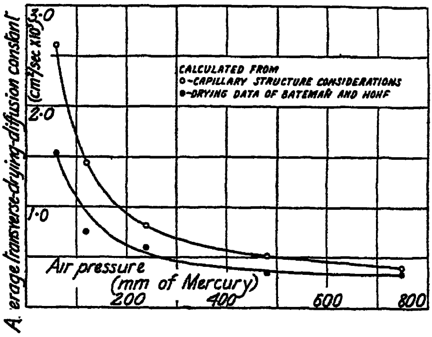

FIG. 7.—Average transverse-drying-diffusion constants relative to unit dimensions of the wood between the fibre-saturation point and the oven-dry conditions, for wood with a swollen-volume specific gravity of 0·365 dried at 40° c. under different reduced air pressures.

A similar analysis for flow in the transverse directions through the heartwood of coniferous woods gives similar results, except that the pressure drop through the pits is still much greater in proportion to that through the fibre cavities than for flow in the fibre direction.[14]

Generally, the movement of a liquid through wood does not occur in a continuous liquid system with free liquid on the entrance and exit faces, as has just been considered. When green wood is dried, or partially dried, or dry wood is treated with a liquid or solution, air-liquid menisci are formed in the wood, which add greatly to the complication of the process. When a piece of completely water-filled wood is dried in air, free evaporation occurs until menisci are formed in the pit-membrane pores of the surface fibres. Further evaporation will occur only when the relative vapour pressure is reduced sufficiently to overcome the added resistance to evaporation caused by the curvature of the menisci in the largest pit-membrane pores. This can be calculated by use of the Kelvin equation.[14] The swelling pressure corresponding to the reduction in vapour pressure can, in turn, be calculated from the swelling-pressure equation.[14] From these equations it can be shown that further evaporation from pit-membrane pores with a radius of 42 millimicrons or less will exert a force great enough to collapse the fibre.[14] Such collapse occurs rarely in commercial drying of wood, and then only in occasional fibres or groups of fibres, because the fibre cavities are rarely completely filled with water and, at the same time, have all of their communicating openings less than 42 millimicrons in radius.

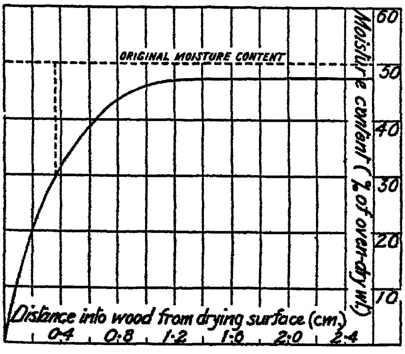

FIG 8.—Moisture-distribution curve obtained after drying normal green sitka spruce for 3·75 hr in the tangential direction at 40° c. and 0 % relative humidity.

Normally, green wood rarely contains more than three-quarters of the amount of water necessary completely to saturate the structure. If the air bubbles in each fibre cavity are larger than the largest communicating pit opening, then free water can move as drying occurs. Tension set up in the pit-membrane pores due to evaporation forces causes the expansion of the bubbles within the fibre cavities and the free flow of liquid. On the basis of correspondence of the fibre-saturation point to a relative vapour pressure of 99 %,[14] the evaporative tension could be 13·5 atm. or more.

The mechanism of the liquid flow will, in general, be as follows. In a series combination of fibre cavities containing equal-size air bubbles, the flow of liquid toward the wet line will occur first from the fibre cavity nearest to the surface, because the distance of the flow, and hence resistance to it, will there be least. The bubble within the fibre cavity will expand, as flow takes place, until it practically fills the cavity. The bubble meniscus will then tend to be pulled into one of the pit orifices. This pull will increase the curvature of the bubble to a point at which the resistance to further expansion exceeds the resistance to expansion of the air bubble in the next fibre cavity. Flow will then occur from this second fibre cavity until its bubble practically fills the cavity. Because of the irregularities of the fibre-cavity surfaces, the bubbles will never conform to the surface, since in doing so the curvature of a bubble in one fibre cavity would be increased to a value greater than that of an air bubble in another fibre cavity in the series combination. The water in the second fibre cavity from the wet line can therefore pass through channels between the bubble and the fibre wall of the first fibre cavity from the wet line. This will increase the resistance to liquid flow, but will not prevent it.

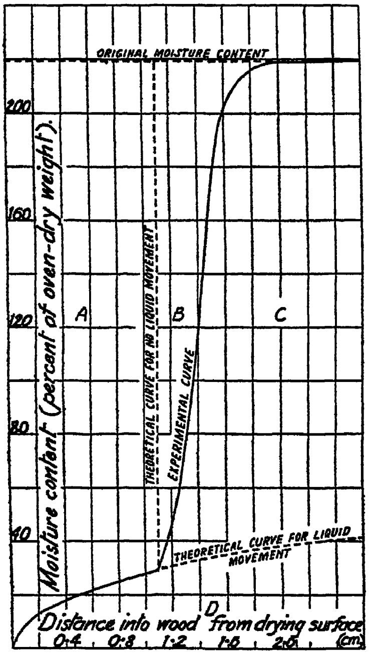

FIG. 9.—Moisture-distribution curve obtained after drying water-saturated Sitka spruce for 259·5 hr. in the tangential direction at 40° C. and 0 % relative humidity.

$\frac{\text{Area } A}{\text{Area } (A + B + C + D)}$ = fraction of evaporable moisture lost if there were no movement of liquid water;

$\frac{\text{Area } (A + B)}{\text{Area } (A + B + C + D)}$ = fraction of evaporable moisture actually lost;

$\frac{\text{Area } (A + B + C)}{\text{Area } (A + B + C + D)}$ = fraction of evaporable moisture lost if there were free movement of liquid water.

The air bubbles in the fibre cavities will vary randomly in size, so that flow may occur first from a fibre cavity an appreciable distance in from the wet line. The bubble in this cavity will, however, have to be sufficiently larger than a bubble in a fibre cavity near the wet line to make up for the difference in flow resistance offered by each distance. As drying progresses, the chance that a bubble, in a fibre cavity at a considerable distance from the wet line, will lose its water by expansion of a contained air bubble before the same loss occurs in a fibre cavity nearer the wet line becomes increasingly remote, because of the greater probability under these conditions that the water will have to flow through more fibre cavities that contain practically completely expanded air bubbles. It is also possible for flow to occur in isolated places in a direction opposite to the moisture gradient because of less resistance to flow. On the average, however, flow will be towards the wet line at which evaporation is taking place, with a predominant tendency for the water nearest the wet line to move first.

Except in the case of green wood that is practically filled with water, the movement of free water when drying wood responds to the diffusion occurring in the outer zone, which is below the fibre-saturation point. If the free water moved either faster or slower than the bound water and the water vapour, the moisture gradient in the zone of transition would decrease or increase so as to make the movement of free water respond to the movement of the water below the fibre-saturation point that is motivated by diffusion. There is, therefore, rarely a break in the curve representing the relationship between moisture content and the distance into the wood from the drying surface. Fig. 8 shows such a normal drying gradient.

When green wood contains sufficient water to fill part of the fibre cavities completely, the free water in these filled fibre cavities will not move as the wood dries. In this case, a moisture gradient of the type given in Fig. 9 will result. In such cases, drying constants cannot be calculated from drying rate or gradient data.

Summary

It is shown that the movement of water through wood can be of three types: namely, water-vapour diffusion through microscopically visible structure, bound-water diffusion below the fibre-saturation point through the cell-wall structure, and free-water movement above the fibre-saturation point through the microscopically visible capillary structure as a result of externally applied pressure or of internal capillary forces.

It is shown that diffusion through wood can be calculated from capillary-structural data, by considering the diffusion through the various capillaries in parallel as additive and the resistance to diffusion through the various capillaries in series as additive in the same manner as electrical conduction.

On this basis, the diffusion of a solute through water-saturated wood is calculated. Agreement between the calculated values and experimentally determined diffusion and electrical-conductivity values is quite good.

In a similar way, drying-diffusion constants are calculated for lamina of different moisture contents, at right-angles to the drying gradient, by combining vapour diffusion through the microscopically visible capillary structure with bound-water diffusion through the cell walls, with both transposed to the same units. Diffusion constants calculated from rates-of-drying and moisture-gradient data agree well with the theoretical values. Previously obtained variations of the diffusion constant according to variations of moisture content are explained.

The resistance to movement of free water through the various types of capillary structure under conditions where no water-air menisci are formed in the wood is analysed. The movement of free water under drying conditions is shown to occur as a result of capillary forces created in the zone of the wood below the fibre-saturation point. This movement is not a true diffusion, but in the case of the drying of green wood, none of the fibre cavities of which are completely filled with water, the movement is such as to make it appear to be a diffusion phenomenon.

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THE PENETRATION OF LEATHER BY WATER AND WATER VAPOUR

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For the purpose of this paper, leather may be considered as a very closely woven "textile," in which the interstices are much smaller than in any artificial woven material. The leathers which will be described are all

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" light " leathers; the so-called " heavy " leathers, such as sole leather, will not be discussed. The arrangement and size of the fibres, and hence of the interstices, varies considerably according to the kind of animal from which the skin has been taken, the position on the animal and the nature of the tanning, pretanning and finishing. The closeness of the " weave " also varies across the thickness of the skin, this being most open on the flesh side, while as the grain (the outer surface of the skin after removal of the epidermis) is approached, the structure becomes more compact and the fibres less easy to resolve with the microscope. Numerous photo-micrographs illustrating the nature and range of this fibre structure are to be found in leather textbooks such as Wilson's *The Chemistry of Leather Manufacture* or the recent volumes produced by the British Leather Manufacturers' Research Association, *Progress in Leather Science*, 1920–1944.

An intercommunicating network of capillary gives access from the grain to the flesh surface of the leather uninterrupted by physical barriers. The size and distribution of these interfibrillar spaces and the nature of the fibre surfaces are the dominant factors in determining the behaviour of leather to water and water vapour. In what follows, a summary will be given of an attempt to assess quantitatively the several capillary factors which make leather so satisfactory as a clothing material. It will be seen that its high porosity (fraction of total volume occupied by air spaces) and the small radius of its capillaries allow it to be given a high degree of resistance to the passage of liquid water while preserving its high water-vapour permeability. The two factors may be combined in such a way as to be exceptionally favourable for certain clothing (e.g., shoe uppers, leather tunics, gloves) where water must be excluded but perspiration allowed to escape.

Water-vapour Permeability

In general, measurements of the water-vapour permeability to be found in the literature are not in a form which allows the results to be expressed in absolute units as diffusion coefficients. This is because the diffusion of water vapour through the leather has been observed under conditions where a boundary layer of non-turbulent air of unknown effective thickness exists on one or either face of the leather. The thickness of this layer will have a time mean value,[1] depending on the wind-speed and the size and shape of the surface.[2,3] Even with considerable wind speeds, thicknesses of the order of 0·25 to 0·5 cm. are to be expected. Thus Penman and Schofield [4] found it to be about 0·25 cm. in experiments involving evaporation from soil in open air. Babbitt [5] in his experiments on fibre board found a residual resistance of the same order. It will be seen, then, that particularly with the more permeable leathers here described (see Table I), which have diffusion coefficients as high as one-fifth of that of the diffusion coefficient of water vapour through air, failure to allow for the boundary layer will give quite misleading results. This conclusion is also reached by Mitton,[6] who found elimination of the boundary layer by a vigorous air flow " surprisingly difficult."

The method to be described was therefore designed to allow the effect of the boundary layer to be eliminated in the calculation. The arrangement was as follows.

A 3-in. circle of leather rested on a 2 % agar gel inside a flat circular tobacco tin, this gel resting on a metal plate under which was a spring keeping the leather pressed against the lid of the tin. A circular hole, 2 in. diam., cut in the lid, determined the area of the leather exposed. A similar tin, containing a gel, but no leather, served as a control. The two were exposed side by side in a constant-temperature room and weighings of each made until the rate of loss of water had remained constant for about two days. The relative humidity of the room was recorded and the thickness of the leather measured after equilibrium had been reached. A value for the diffusion coefficient through the leather was then calculated by assuming that the effective thickness of the surface boundary layer of air, through which the water must diffuse to reach the turbulent air of known partial vapour pressure existing in the room, was the same over the gel in the control tin as it was over the leather. The vapour pressure on the side of the leather in contact with the gel was taken to be that of water, since the effect of the 2 % high-molecular-weight agar would be negligible. In making the calculation, it is assumed that the rate of transfer across any section is proportional to the concentration gradient at the section, and that the constant of proportionality (i e., the diffusion coefficient) is constant throughout the thickness ; that is, that Fick's law holds. As in fact the value of D, the diffusion coefficient, will not be constant throughout the thickness the result obtained will be a weighted mean. The rate of evaporation was determined correct to 1 %, and the diffusion coefficients obtained were reproducible to within 10 %.

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[1] Brunt, *Physical and Dynamical Meteorology* (1934), p. 261.

[2] Powell and Griffiths, *Proc. Inst. Chem. Eng.*, 1935, **13**, 175.

[3] Powell, *Proc. Inst. Chem. Eng.*, 1940, **18**, 36.

[4] Penman and Schofield, *J. Agric. Sci.*, 1931, **31**, 102.

[5] Babbitt, *Can. J. Res. A*, 1939, **17**, 15; *Can. J. Res. A.*, 1940, **19**, 90.

[6] Mitton, *J. Int. Soc. Leather Trades Chem.*, 1947, **31**, 44.

TABLE I—FULL-CHROME LEATHER

Leather	l (cm.)	t (° c.)	R.H. (%)	Porosity S	% Moisture at Equilibrium	$W_0 \times 10^6$	$W \times 10^6$	D_0	D	$\frac{D}{D_0S}$
B Army upper leather .	0·292	21·4	62	0·382	22·0	3·56	0·972	0·254	0·054	0·56
G Army upper leather .	0·274	21·4	62	0·325	20·2	3·56	0·77	0·254	0·037	0·49
I Army upper leather .	0·295	21·4	62	0·357	24·4	3·56	0·667	0·254	0·034	0·38
K Army upper leather .	0·295	21·4	62	0·280	22·6	3·56	0 667	0·254	0·034	0·48
R Side, not embossed .	0·302	21·4	62	0·350	23·8	3·56	1·21	0·254	0·060	0·68
S Side, not embossed .	0·282	21·4	62	0·375	23·0	3·56	1·17	0·254	0·068	0·68
T Side, embossed .	0·250	22·4	40	0·402	29	6·67	1·64	0·257	0·045	0·45
U Side, embossed .	0·282	20·7	66	0·390	21	3·00	0·814	0·253	0·051	0·52
V Side, embossed .	0·249	24	54	0·387	20·7	3·00	1·59	0·258	0·058	0·57
W Side, embossed .	0·086	21·1	61	0·390	19·2	2·92	0·967	0·253	0·054	0·65
X Box calf . . .	0·070	21·1	61	0·405	35·8	2·92	2·06	0·253	0·067	0·65
Y Goat . . .	0·071	24·0	54	0·405	38 0	5·00	3·49	0·258	0·081	0·78

It was to be expected that the value of the porosity would largely determine the diffusion coefficient for a particular leather. Penman [7] has shown that the diffusion of gases through granular systems such as soils, sand and glass beads having porosities less than 0·7 is determined by the equation, $D = 0{\cdot}66SD_0$ where S is the porosity, D the diffusion coefficient of the gas in the granular system and D_0 its diffusion coefficient in air. The constant 0·66 is an inverse measure of the tortuosity of the path which the gas has to take. It was of interest to see what values would be found for leather in place of this constant, in the hope that this would throw light on the mechanism of the diffusion.‡

Porosity determinations were, therefore, made at the end of each experiment on the leather which had reached equilibrium. The weight of the leather in air (a), in paraffin (b) (air being removed by evacuation at a pressure not low enough to cause loss of water), and again in air when still impregnated with paraffin (c), were determined. The porosity is then given by $\frac{c - a}{c - b}$. In making this determination, the assumptions are made that all the air spaces are filled with paraffin and that the leather does not swell in this liquid.

In Table I a number of results obtained for full chrome leathers are given. W_0 is the weight of water evaporating from the free gel surface in g./cm.^{2}/sec., and *W* the corresponding amount evaporating through the leather. It will be seen that the values of D are about one-fifth of the value for the diffusion coefficient of water vapour through air (D_0). In the final column are given the values for $\frac{D}{D_0 S}$. These range from 0·38 to 0·78, the average value being 0·55 as compared with 0·66 for Penman's granular systems.* Considering what a much more complicated and varied geometrical system leather presents, the closeness of the agreement is of considerable interest and suggests strongly that the mechanism of diffusion is simply that of gaseous diffusion through the interfibrillar air spaces, while any diffusion through the fibres themselves is small. Mitton also comes to a similar conclusion, although he finds much lower values for $\frac{D}{D_0}$. In the case of vegetable-tanned hide belly leather, he claims the diffusion through the "fibres is not entirely negligible." Since he gives no experimental determinations of porosity, it is impossible to say how much the lower $\frac{D}{D_0}$ values are due to failure to remove completely the effect of the boundary layer of air, and how much to the porosity being lower than in our experiments. (The porosity which we are concerned with in the equation is, of course, that of the leather after it has taken up water to the equilibrium condition.)

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[7] Penman, *J. Agric. Sci.*, 1940, **30**, 437, 570.

‡ The interest of comparing the results obtained with leather to Penman's relationship for granular systems was pointed out to the writer by Dr. R. K. Schofield in 1941. Since this research was completed Dr. Mitton's paper [6] appeared, where the relationship is also discussed, but where no measurements of porosity are given.

TABLE II—SUMMARY OF DIFFUSION RESULTS

Type of Leather	No. of Leathers	Range of Grease (%)	Range of D	Average D	Range of $\frac{D}{D_0 S}$	Average $\frac{D}{D_0 S}$
Full-chrome leather	11	—	0·034 –0·068	0·048	0·38–0·71	0·55
Full-chrome ; dubbin added in Lab. .	13 treatments	5·6–23·8	0·0030–0·025	—	0·09–0·55	—
Semi-chrome Service upper leathers .	11	11·8–22·1	0·0077–0·035	0·0194	0·13–0·55	0·33
Service chrome with high grease content	3	18·9–29·6	0·0054–0·015	—	0·20–0·41	—
Vegetable leather with high grease content	2	26·2–28·8	0·0016–0·0045	—	0·21–0·32	—
Patent leather	4	Low	0·0006–0·0019	0·0011	—	—

In Table II a summary is given of all the leathers examined. These include a number of leathers where the grease content is much higher than in the full chrome leathers of Table I, where it is of the order of 2 %. The value of $\frac{D}{D_0 S}$ is not only lower in these leathers but was found to be more variable. This is probably because the grease is unevenly distributed, and so, instead of merely reducing the porosity, it also blocks some of the channels in the capillary network and so lengthens the path which the vapour has to traverse. Patent leather is included as an example of a leather whose surface is sealed with a layer of material of very low permeability. The effect of water-pigment finishes in reducing the permeability is considerably less than this.

Penetration Pressures

Ordinary vegetable-tanned leather is easily wet by water. On the other hand, leather can be prepared, for example, by chrome tanning, so as to be "non-wettable," that is to say, having a high contact angle against water.

If we consider the interfibrillar spaces as equivalent to capillaries, and if θ is the contact angle made by the air-water interface against the wall of the capillary (the angle being measured in the water), then, where θ is greater than 90°, the capillary *depression* will be given by $\frac{2\gamma \cos \theta}{g\rho r}$ where γ is the surface tension, r the radius of the capillary, ρ the density of water. So before water can enter the leather capillaries a pressure has to be exerted which exceeds the pressure of a column of water of this height. It is possible to measure this penetration pressure, as in the case of textiles, and to use the values obtained as an indication of the degree of water-repellency. Leather, however, unlike evenly woven textiles contains capillaries of different sizes and the radii of these vary throughout their length. The penetration pressure will, therefore, be determined by the diameters of the "bottle-necks" in the largest capillaries.

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* In calculating the diffusion coefficients it was assumed that the temperature of the gel and leather surfaces was the same as the room temperature. Actually the temperature of these surfaces will be between this and the wet bulb temperature. The error thus introduced will not be large enough to effect any of the conclusions drawn in this paper, but it may be considerable for leathers of very low resistance, such as *W*, *X*, and *Y* of Table I.

To measure the penetration pressure, a 2-in. circle of leather was clamped in a horizontal position in a simple apparatus which was constructed from a brass gas union. Pressure was applied to the water on the lower side of the leather by increasing the height of a column of mercury by 2 cm. per minute. (With some leathers, such as those heavily stuffed with grease, it was found necessary to apply the pressure more slowly to obtain results which were independent of the rate.) The pressure at which the first six drops appeared on the upper surface of the leather was taken as the penetration pressure.

For full chrome leather, penetration pressures of 15 to 25 cm. of mercury frequently occur, but values as high as 40 cm. have been found. Such figures are much higher than those of ordinary textiles, and are possible because of the small radius of the leather capillaries. Generally, no directional effect was found, the same result being obtained whether the water entered from the grain or the flesh side. Measurements were generally made with the water entering from the flesh side, in which position leaks round the side could be more easily prevented and the appearance of drops on the smooth grain side could be better observed. In some leather, however, a considerable directional effect was found. The largest effect found was with a chrome-tanned side which gave 40 cm. Hg from grain to flesh and only 20 cm. from flesh to grain. For a particular method of tanning, if pieces from the same skins are used, it is found that the penetration pressure increases with the chromium content.[8] True penetration pressures (in one particular case) were only reached with 2·75 to 3·0 % Cr_2O_3, while increasing the Cr_2O_3 content from 3 to 7·5 % increased the penetration from 12 to 20 cm. Hg. The pressures obtained depend also on the method of tanning used. An extreme example was found by Pressley,[9] who showed that, if great care was taken to remove all free fatty acid from the pelt, it could be tanned under conditions which would give 5·75 % Cr_2O_3 with the normal pelt and yet show no degree of water-repellency. Apparently a minimum of about 0·5 % free fatty acid on the weight of the skin is necessary, but further amounts have little effect.

Vegetable-tanned leathers, which are normally easily wettable and show a negative penetration pressure, can be given a high penetration pressure by treating with aluminium soap. By treating vegetable-tanned Cape sheep-skins in this way, penetration pressures in the neighbourhood of 20 or 30 cm. Hg were obtained (Robinson and Beakbane, unpublished). This amount of aluminium which it was necessary to deposit before high penetration pressures were reached, was found to be considerably in excess of the amount to convert all the fatty acid used to aluminium soap.

Treating chrome-tanned leather with aluminium soap may improve the water-resistance properties even where the penetration pressure is not greatly affected. This will be discussed in a later section.

If grain and flesh splits from the same skins are tested, higher penetration pressures are, as would be expected, obtained with the more compact grain region. An interesting exception to this was found with a horse hide, where by removal of too much of the flesh side, very low penetration pressures were obtained (2 cm. Hg). The explanation was that the hair follicles (which are exceptionally deep in some parts of the horse's hide) had been severed, and since the radii of these follicles are much larger than the radii of the largest interfibrillar capillaries, the penetration pressure was reduced by some ten times.

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[8] Bowes, Davies, Pressley and Robinson, *J. Int. Soc. Leather Trades Chem*, 1947, **31**, 236.

[9] Pressley, *J. Int. Soc. Leather Trades Chem.*, 1946, **30**, 94.

Rates of Flow

The radius of interfibrillar capillaries cannot be directly observed as in a textile, and even the effective radius, which determines the penetration pressure, cannot be calculated unless a value for the contact angle is obtained (this will be discussed later). However, by determining rates of flow under conditions where Poiseuille's law holds, it is possible to obtain a measure of $\frac{nr^4}{l}$, where n is the number of capillaries per unit area, r is their apparent mean radius and l the length. Where the thickness of the leather is constant, or is allowed for, and where n is not varied (e.g., where positional effects can be allowed for), changes in the rates of flow may be interpreted as changes in the capillary radius.

TABLE III—RATES OF FLOW AND PENETRATION PRESSURES

No.	Leather	Pressure used (cm. H_2O)	Thickness (mm.)	Rate cc./min./mm. at 50 cm. H_2O	Penetration Pressure (cm. Hg)
	Full-chrome :				
20	Box side	25	3·12	16·8	19·5
4	Willow side . . .	50	1·6	8·32	18–23
21	Side	50	1·93	3·3	—
1*a*	Side, heavily stuffed . .	50	2·85	0·51	38
1*b*	Side, degreased . .	50	3·0	0·043	23–28
22	Goat	50	1·3	4·94	10
22*a*	Goat, glazed . . .	50	1·3	1·30	11
	Semi-chrome :				
23	Split hide . . .	50	2·9	7·25	—
24	E.I. kip	50	8·55	8·55	5·5–6·5
25	Butt, unstuffed . .	50	2·94	9·1	10
26	Butt, stuffed . . .	50	2·73	1·83	16–23
6*b*	Buffalo side . . .	50	3·09	1·20	13
6*a*	Buffalo side, heavily stuffed	50	2·85	0	—
	Vegetable-tanned :				
27	Split hide . . .	50	2·65	7·95	Negative
28	E.I. kip	30	2·18	7·2	Negative
29	Unfinished calf . .	50	2·25	12·2	Negative
30	Sheep (gasmeter leather) .	25	0·90	3·75	15·0
	Full-chrome gloving :				
31	Horse	50	2·23	47·5	2–6
32	Cow	50	1·95	47·0	4–6
8*a*	Domestic sheep . .	50	1·75	258	1
33	Cape sheep . . .	25	1·00	19·4	4–8
	Semi-chrome gloving :				
11	Persian sheep (proofed) .	50	1·50	86·0	4–6
11*ap*	Persian sheep (proofed), grain split	50	0·75	49·2	3·5
11*bp*	Persian sheep (proofed), flesh split	25	0·70	406	—
34	E.I. sheep, grain split .	50	0·78	5·45	—
34*b*	E.I. sheep, flesh split .	12·5	0·77	98·6	—
35	E.I. sheep . . .	25	1·00	4·67	11·5
36	E.I. sheep (gasmeter leather)	25	1·20	2·1	17·0

For these determinations the rate of flow must be uncomplicated by the presence of air-water interfaces. Air in the leather capillaries was therefore completely removed by immersing overnight in water under reduced pressure. With some leathers wetting was aided by a small amount of Lissapol C. The leather was then placed in a modified form of the apparatus used for the penetration pressures, in which *both* sides of the leather were in contact with water.

When pressure was applied and water flowed through to the top surface of the leather, it was arranged that this water overflowed into a measuring vessel. The results were carried out at about 18° c. As we are dealing with values which vary by many times, temperature control was unnecessary. On plotting rates of flow against pressure, for both full chrome- and vegetable-tanned leather, no deviation from a straight line within the experimental error was found with pressures up to 50 cm. water (higher pressures were not investigated). It was assumed, therefore, that Poiseuille's law holds for this range of pressure. The rates obtained were found to be reproducible. Since the leather was immersed overnight in water, the rates obtained are determined by the size of the capillaries where the fibres are swollen to their equilibrium condition.

In Table III rates of flow, in cc./min. at 50 cm. water pressure are given for a wide variety of light leathers. The disc of leather was 2 in. diam. in all cases. In the 5th column is given the rate multiplied by the thickness, which might be expected to be nearly proportional to nr^4. Finally, in the last column, the penetration pressures are given for adjacent pieces of leather.

It will be seen that a very large range of rates of flow were obtained. The low results obtained with the stuffed leathers (i.e., those which had been drummed with molten grease) were to be expected as a consequence of the capillaries being partly filled with grease (compare corresponding decreases in porosity and water-vapour diffusion shown in Table II for other stuffed leathers). The high rates obtained with gloving leather are indicative of the effects of choice of tannage, pretannage and skins in this very supple form of leather.

As with penetration pressures, a directional effect was found. Eight pieces of full-chrome calf were tested grain to flesh and eight flesh to grain, all being taken from the same skin, randomised and tested once only. The average rate, flesh to grain, was 11·9 and grain to flesh 7·3. The standard errors were 2·17 and 1·60 respectively (due largely to positional effects). Repeated testing of the same piece of leather reduced the rate of flow.

The variation of the rate of flow for different positions in the same skin was smaller than might have been expected, e.g., 11·0 to 2·0 cc./min. On the other hand, as will be seen from Table III, the rates for different skins, even when uncomplicated by stuffing, differ by as much as 200 times. The rate of flow through a grain split is very much slower than for a flesh split from the same skin. Thus (for a semi-chrome E.I. sheep-skin) the ratio of the average rate of flow for the flesh split to the average for the grain split was 19·4 to 1. If it is assumed that both splits contain the same number of capillaries (a rather crude oversimplification) this would mean that the average radii of flesh and grain capillaries would be in the ratio of 2·1 to 1 (actually the "capillaries" get much narrower as they approach the grain surface).

From these brief remarks it will be seen that measurement of the rate of flow is a useful simple test for mapping the surface of skins and expressing their "openness" in figures.

Contact Angles

Sometimes when two leathers of approximately the same, fairly high, penetration pressure are compared, it is found that one is more easily wettable than the other when judged by some other test. (For instance, if a jet of water is allowed to impinge on the surface of the leather, the time required to wet the surface may be much longer for one than for the other. It was thought that measurement of advancing and receding contact angles might help to explain this. Preliminary measurements showed that advancing contact angles as high as 160° could be attained with leather. Since the contact angle of water against paraffin wax is only 108°,[10] it seems that these high angles can only be explained by the theory of Cassie and Baxter[11] who have shown that very high *effective* contact angles can be obtained for a grid-like structure as in the case of a duck's feather. They showed that if the grid is composed of cylindrical fibres of radius r, and if $r + d$ is half the distance between their centres, then, for a given fibre contact angle θ_A, the effective advancing contact angle θ_D will become higher as $\frac{r+d}{r}$ increases. A similar relationship holds for the dependence of the effective receding contact angle θ_W on the receding contact for the fibre θ_R and $\frac{r+d}{r}$. In this way not only can high values θ_D be accounted for, but also values of θ_D above 90°, even when θ_A is below 90°. Cassie and Baxter applied the theory to woollen yarns and it would seem that the same explanation must apply, qualitatively, to leather.

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[10] Sumner, *Wetting and Detergency*, (Harvey, 1937), p. 45

[11] Cassie and Baxter, *Trans. Faraday Soc.*, 1944, 40, 546.

The method of measuring the contact angles was essentially the plate method of Adam and Jessop, with the important difference that when measuring advancing and receding angles greater than 90°, the point of rotation of the arm to which the strip of leather was attached was *below* the level of the liquid, while for angles of less than 90° it was above the liquid. This allows all advancing angles to be measured when the leather is entering the water on rotating the arm, and all receding angles when the leather is leaving the water. The angles were read to the nearest 5°. Angles lower than 15° could not be read.

TABLE IV—CONTACT ANGLES AND PENETRATION PRESSURES

No.	Leather	Advancing Contact Angle (degrees)		Receding Angle (degrees)			Penetration Pressure (cm. Hg)
		Grain Surface	Flesh Surface	After 2 min.	After 10 min.	After 20 min.	
	Full-chrome:						
1*a*	Heavily stuffed side	105	150	*ca.* 90	80	70	18, 21
1*b*	Heavily stuffed side, degreased	140	150	20	20	20	31·5
4	Willow side, unfinished	120	160	<20	<20	<20	21·5, 20
4*p*	Willow side, proofed	130	160	45	30	30	25·5, 25
5	Calf, unfinished	130	160	30	<20	<15	15·5, 15·5
5*p*	Calf, proofed	140	165	60	45	40	21, 23
	Semi-chrome:						
6*a*	Buffalo, very heavily stuffed	105–110	60	60	50	40	—
6*b*	Buffalo, not stuffed	120	35	35	30	20	13·0
6*c*	Buffalo, degreased	105	20	25	20	20	—
	Full-chrome:						
8	Domestic sheep	90	160	30	<20	<15	1·0, 1·0
8*p*	Domestic sheep, proofed	125	165	40–35	30–25	25	10·5, 11·0
	Cape sheep, 5 % fat liquor, thus:						
10*a*	65 % mineral oil, 35 % sulphated cod oil	120		50	40–30	40–25	13, 16
10*ap*	65 % mineral oil, 35 % sulphated cod oil, proofed	150		75–70	60–65	50	13·5, 18
10*b*	100 % sulphated cod oil	130		40	25	<15	7·0, 11
10*bp*	100 % sulphated cod oil, proofed	140		60–75	55–65	40–55	11, 17
10*c*	10 % sodium oleate, 90 % neutral cod oil	135		40	40	40	5, 7
10*cp*	10 % sodium oleate, 90 % neutral cod oil, proofed	150		60–75	60–65	50–55	—
	Semi-chrome:						
	Persian sheep, thin grain split (proofed):						
11*ap*	Grain surface	130		60–70	45	40	—
11*bp*	Flesh surface	160		>90	—	25–20	—

Baxter and Cassie [12] recommend that a measurement of the rate of fall of the effective receding contact angle with time as a test of the water-repellency of yarns. In their test the yarn was withdrawn slowly from the water by a highly geared mechanism and the time required for the angle to reach 90° was noted. Such an apparatus was not available, but some measurements of receding contact angles after 2, 10 and 20 min. immersion were made. The drop in receding contact angle to comparatively low values which is found here, and which was observed by Baxter and Cassie, is due to film formation across the air spaces between the fibres. Baxter and Cassie liken this to the formation of a film of water across a small wire loop, the stability of which will depend on the value of the receding contact angle and its area. Whether or not a film forms on such a loop is found to depend on the time of immersion. If, after a certain time of immersion, films form, bridging the spaces between the fibres of a yarn, the effective receding contact angle will drop to a value below that of the receding contact angle for this fibre, as the air-fibre grid is replaced by a water-fibre grid. This seems to be also the mechanism in the case of leather.

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[12] Baxter and Cassie, *J. Textile Inst.*, 1945, **36**, 167.

In Table IV, advancing and receding contact angles are shown for a number of leathers, together with the corresponding penetration pressures. Each of the values given is the average of at least three readings obtained from separate pieces cut from adjacent positions in the skin. A number of points, all in accordance with the assumption that the qualitative aspects of Cassie and Baxter's theory hold for leather, are brought out on examining these results

(1) The advancing contact angles are much higher than could be accounted for without Cassie and Baxter's theory.

(2) The flesh side of the leather always showed higher advancing contact angles than the grain. This can be understood since the more open structure of the flesh side would give rise to a higher effective contact angle. Similarly, "buffing" the grain (removing the smooth surface by abrasion) increases the advancing contact angle.

(3) Putting a large quantity of grease into the leather decreased θ_D, while the removal of a large quantity of grease increases it. This effect is evidently due to the grease filling the interstices and so reducing the effect of structure in increasing θ_D.

(4) In all cases where the advancing contact angle was high the receding contact angle was much lower. Treating leather with aluminium soap (referred to in Table IV as proofing) as well as somewhat increasing the advancing contact angles had a marked effect in decreasing the fall in the receding contact angle with time. These treated leathers were much more resistant to wetting (as judged, for instance, by the jet test). Quite apart from any possible practical value of the aluminium soap treatment itself, the results indicated that the measurement of the fall of receding contact angle with time would be a useful test for water-repellent leathers.

The high advancing contact angles for flesh side and "buffed" grain side are not an indication of these surfaces being more water resisting, and it is much easier to wet the flesh surface by rubbing in a drop of water. This is due to film formation taking place more readily amongst the more widely spaced fibres and leading to progressive penetration of the water. This is in accordance with the more rapid fall of the receding contact angle and the greater rates of flow shown by a flesh split.

No one test then seems to be able to assess the water resistance of leather, but measurements of penetration pressure, rates of flow and contact angles can give a very good indication of how the leather will behave.

Behaviour of Single Drops

A good deal of information can be obtained by gently placing single drops of water on the surface of leather. The shape taken up will depend on the contact angles and, if the leather is tilted, the drop in running down the slope will assume a shape which is determined by both advancing and receding angle. These angles can be estimated to, say, 15°. This may be illustrated from some of the leathers described in Table IV.

8 and 8*p*.—A drop on 8 at first shows a contact angle greater than 90°, but this falls rapidly and the drop wets the leather. The penetration pressure is here negative. With the proofed leather, 8*p*, a drop remains on the surface and continues to show an angle greater than 90°. On tilting, it runs down showing a receding angle of 35°.

10*a* and 10*b*.—A drop remains on 10*b* without darkening, but pushing it gently to one side at once causes darkening beneath it. This is in accordance with the low receding contact angle which can be seen on tilting. The ease of wetting is greater than would be expected from the penetration pressure. 10*a* shows no wetting, even when disturbed, and a higher receding angle when tilted than 10*b*. There is no darkening in its wake as with 10*b*. On proofing 10*b* (10*bp*) it behaves as 10*a*.

11*ap* and 11*bp*.—The contrast of flesh and grain surface is here instructive. On the grain surface, 11*ap*, a drop does not wet, even when it is gently rubbed.

The receding angle shown by tilting is not greater than 90°. On the flesh surface, 11*bp*, the drop rolls rapidly down the surface like a drop of mercury on glass, showing that the receding angle is greater than 90°. This "pearling" does not, however, mean that the leather is more difficult to wet, for on gentle rubbing the drop at once enters the leather, leaving a wet surface. The explanation can again be found in Table IV. Since the *initial* receding angle is greater than 90° the drop rolls rapidly off, and the drop does not wet, since the time of contact is not long enough. This higher initial receding angle is presumably due to a higher value of $\frac{r+d}{r}$ than on the grain surface. On the other hand, the easier film formation on the flesh surface allows the drop to be rubbed in more easily than on the grain surface, thus corresponding to the greater fall in the receding angle.

The general impression, then, obtained from the evidence at present available, is that for a leather to be most water resistant, it must not only have a high penetration pressure (which is favoured by a high *advancing* contact angle and small radius of the capillaries), but a high *receding* contact angle which does not decrease rapidly with time. It would seem that measurements of the receding contact angles, and their rate of decrease, may prove in future to be of value in supplementing penetration-pressure measurements. But even if such quantitative measurements are not made, careful observation of the behaviour of drops on the surface of the leather will greatly reduce the chance of misleading conclusions being drawn from the penetration-pressure measurements. When supplemented with such observations, the penetration-pressure determination remains the best single test at present available for the water resistance of light leathers.

We wish to thank the Director and Council of the British Leather Manufacturers' Research Association for permission to publish this paper.

GENERAL DISCUSSION

Dr. D. J. Crisp (*Cambridge*) said: By a slightly different treatment to that given by Dr. Cassie in his opening remarks, Dr. Thorpe and I have shown [1] that the penetration pressure theoretically required to force a liquid between an array of cylindrical hairs or rods is positive as long as the contact angle θ is finite, but tends to zero as θ approaches zero.[1 2] In practice, however, this is unlikely to be true because such an array must be supported below, and any point of contact of the cylinders with supporting structures is bound to be a point of weakness tending to draw the meniscus down and to cause spontaneous wetting before θ reaches zero.

It should also be noted that if the rods are irregularly spaced, the minimum pressure required to wet the fabric will be that derived from the application of eqn. (18) and (19) [2] to the *largest* spaces separating the cylinders; hence the most efficient system for a given number of hairs per unit length will be the regular one with equidistant hairs.

However, another important factor is involved here. If forces are resolved horizontally in Fig. 3 [2] it will be noted that there is a force, $\Delta pr(1 + \sin\beta)$ acting along AB on each side of the hairs. These forces are normally balanced. If one of the hairs is displaced towards another while the penetrating pressure Δp is maintained constant, the radius of curvature R is also constant, and the angle β will diminish with l. Hence the force on this side of the hair decreases, while it increases on the other side, with the result that the hairs are drawn together. In other words, if displaced beyond the limits of the normal elastic restoring force, the system is unstable and the hairs tend to clump together, weakening the water resistance. It is therefore necessary to consider the rigidity as well as the spacing of hairs in assessing the waterproofing qualities.

[1] Thorpe and Crisp, *J. Expt. Biol.*, 1947, **24**, 256.

[2] Crisp and Thorpe, this Discussion.

It is interesting in this connection that one of the groups of waterproofed plastron-bearing insects, the Elmidæ, have rather flexible hairs which can be seen readily to mat together in this way. The insect spends considerable effort overcoming this tendency by combing or grooming the hairs into a regular pattern.[3]

Dr. W. W. Barkas (*Princes Risborough*) said: Dr. Cassie has shown how the penetration pressure of water through a fabric is finite for all angles of contact between 0° and 180° and that there is no special importance to be attached to the 90° contact angle. In the figure he has drawn on the board Dr. Cassie represents the cross-sections of two fibres by circles and shows the position of the meniscus for 0° and 180° contact angles. Will Dr. Cassie explain what happens when there are three fibres (i e. two spaces)? Do not the menisci from the two holes coalesce at a contact angle of 90° and thus give penetration there?

Dr. A. B. D. Cassie (*Leeds*) said: In reply to Dr. Barkas the ideal of equally spaced fibres in one plane is seldom, if ever, attained in practice. Penetration always occurs between two fibres with an abnormally large spacing, so that the penetration pressure is virtually determined by the system discussed in the paper.

Dr. G. S. Hartley (*Harston*) said: With regard to Dr J. M. Preston's remarks on migration of water during the drying of a textile fabric, I agree with Dr. Barkas that thermal migration seemed the most likely explanation of liquid flow to the hot plate.

Mr. D. K. Ashpole (*Bocking*) said: The "critical" moisture values obtained when drying textile materials have been mentioned by Dr. J. M. Preston, and Dr. Barkas has referred to the moisture sorption characteristics of wood and has indicated that he expected the hysteresis loop to be open at saturation. I should like to add to the Discussion on these points.

Figures quoted for the saturation regain * of textiles, and in particular viscose, show very considerable difference from the values of the moisture absorbed from liquid water (the "imbibition" value). The maximum saturation regain value obtained by Urquhart and Eckersall[4] for viscose was 46 % whilst the swelling in liquid water is generally given (e.g. Hermans [5]) as about 90 to 100 % moisture absorption on the dry weight. These large differences must represent failure in obtaining a completely saturated atmosphere when claimed, since it is thermodynamically impossible to have different amounts of moisture absorbed from the saurated vapour phase and liquid water.

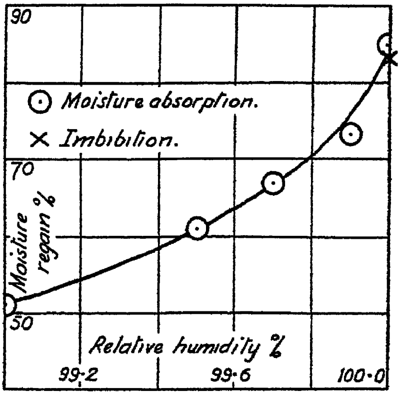

FIG. 1.

Experimental work (which is being continued) carried out in these laboratories † has confirmed this obvious conclusion. The equilibrium moisture absorption for viscose has been determined at several points in the 99·0 to 100·0 % R.H. range by a new technique taking special precautions to maintain constant temperature and at the same time providing conditions for an optimum rate of diffusion of vapour between the water surface and the viscose fibres. The maximum cyclic variation of temperature was of the order of 4×10^{-4} °C. The results obtained are given in Fig. 1. It may be seen that the curve obtained is quite smooth and cuts the ordinate at 100 % R.H. sharply with no tendency to be asymptotic.

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[3] Thorpe and Crisp (in preparation).

[4] Urquhart and Eckersall, *J. Text. Inst.*, 1932, **23**, T163.

[5] Hermans, *Contributions to the Physics of Cellulose Fibres* (Elsevier, 1946), p. 6.

* The regain is the moisture held expressed as a percentage of the dry weight.

† Textile Research Laboratories, Courtaulds Ltd., Bocking, Braintree, Essex.

The value of 85 % as the true saturation absorption regain for the viscose sample used was checked against the imbibition value by a method standardised in these laboratories. Approximately 0·5 g. of dry viscose is soaked in distilled water for 10–15 min. and then centrifuged in a closed tube over water at 1000 **g.** for 5 min. The values of imbibition so obtained repeat within ± 1 % moisture. The imbibition value obtained in this case was 83 %. These results not only show the agreement between the moisture absorbed from the saturated vapour and liquid phases but also show that the hysteresis loop must close at saturation.

The actual figures quoted will only apply to the particular sample of viscose used in these experiments since the imbibition is modified by the history of the sample subsequent to spinning, especially the manner in which, and the number of times, it has been dried. Special treatments (e.g. a urea-formaldehyde, crease-resist treatment) can reduce the imbibition—and the saturation regain—to about 35 to 40 %.

The results of this investigation completely clear up the much quoted[6 7 8] anomaly known as Schroeder's[9] paradox. This phenomenon concerns the observed loss in weight of a gel, which had been swollen in liquid water, when it was placed in the so-called saturated vapour space over liquid water.

Another point which is clarified as a result of this investigation is the work carried out by Preston and Chen[10] on critical moisture contents. In Fig. 2 of their paper they plot the variation of temperature with time of a flannel being dried by radiant heat. After an initial temperature rise corresponding to heating conditions, the temperature remains fairly constant for a period, after which it again rises steeply until the fabric is completely dry when it reaches a new higher constant value. They consider the critical moisture content to have been reached at the intersection of the straight lines drawn through the lower temperature plateau and the second temperature rise period. The actual temperature curve plotted shows no sharp break but a smooth curve joining the two straight portions. This is a real effect and the point (if it could be found) at which a deviation from the linear plateau occurred would represent the true critical moisture condition corresponding to the true saturation regain The correspondence noted by Preston and Chen[18] between their figures for critical moisture content and the previously published saturation regains is largely fortuitous.

Dr. W. W. Barkas (*Princes Risborough*) said: Mr. Ashpole rightly stresses the importance of the surrounding vapour pressure in determining the drying which will result from centrifuging hygroscopic solids. It is none the less possible to remove adsorbed water as well as capillary water from these materials by centrifuging even in a saturated atmosphere, because the compressive stress set up in the solid, when it is forced against the end of the tube, is sufficient to raise the vapour pressure of the material above saturation. It therefore loses moisture and after removal from the centrifuge exerts a vapour pressure less than saturation. Conversely, if a solid is centrifuged when attached at the end nearer the axis (as in a wooden air-screw) it will be in tension and tend to adsorb moisture from the surrounding air. In both cases the moisture content decreases with increasing distance from the axis and does not change at the free end. If the solid is coated with an impervious skin, a redistribution of moisture will occur without exchange from the outside air. The ordinary theory of centrifuging, which deals with particles suspended in a liquid, is not sufficiently general to cover the centrifuging of hygroscopic gels.

Dr. R. K. Schofield (*Harpenden*) said: I have no reason to doubt that ordinary mineral soil can be brought to complete saturation from the vapour phase.

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[6] Freundlich, *Colloid and Capillary Chemistry*, 1926, p. 672.
[7] Katz, *Trans. Faraday Soc.*, 1933, **29**, 283.
[8] Bancroft, *J. Physic. Chem.*, 1912, **16**, 395.
[9] von Schroeder, *Z. physik. Chem.*, 1903, **45**, 109.
[10] Preston and Chen, *J. Soc. Dyers Col.*, 1946, **62**, 361.

Dr. Davidson and I observed uptake from an atmosphere at 99·97 % R.H. by salt-free soil that had been saturated and drained with the aid of a "suction" of 1 atm. It was confirmed that this sample was in equilibrium with an atmosphere of 99·93 % as required by thermodynamics. In the case of mineral soils the contact angle appears to be zero or very small. I think it is only when the contact angle is zero that we can argue from thermodynamics that the state of saturation must be the same whether this is obtained by absorption from the vapour or the liquid (air and other gases being excluded) At the same time, I share with Mr. Ashpole the suspicion that many statements found in the literature are unreliable on account of faulty experimental technique.

Mr. D. K. Ashpole (*Bocking*) (*communicated*) : Dr. Barkas correctly observes that the imbibed moisture as distinct from the surface water can be removed by the hydrostatic pressures produced in centrifuging. This effect is the corollary of the swelling pressure which was first put on a quantitative basis by Katz [11] in 1918. The conditions of centrifuging were so chosen in our standardised procedure that the maximum reduction of absorbed moisture due to the hydrostatic pressure is only of the order of 1–2 % as calculated from the equation given by Katz.[11] Hence the agreement of the imbibition by centrifuging and the true saturation absorption as obtained in our experiments to within 2 % moisture goes far to substantiate the postulation that the hysteresis loop closes at saturation.

Dr. W. W. Barkas (*Princes Risborough*) (*communicated*) : In reply to Mr. Ashpole, I do not agree that "it is thermodynamically impossible to have different amounts of moisture absorbed from the saturated vapour phase and liquid water." Firstly if, as a result of wetting, the material suffers an irreversible change, it may have a different equilibrium moisture content, just as a lump of putty can support the same load at different equilibrium displacements if it has suffered a plastic deformation (from any cause) between successive readings. This is not the case for a lump of elastic steel. Secondly, hysteresis in sorption is now generally recognised as an empirical reality no matter how much we may squabble about its explanation. None the less, can it not equally well be argued that it is "thermodynamically impossible" for different amounts of water to be sorbed at any single vapour pressure other than saturation ?

Thermodynamics can be applied to irreversible as well as reversible sorption systems provided an elastic substance of known compressibility, such as water vapour, is used for measuring the work done ; just as the work done in the plastic deformation of putty can be measured, provided an elastic spring of known compressibility is used for measuring the applied stresses. It is the spring, not the putty, that we must be able to return to its initial state.

This is not intended to cast doubt on the results of Mr. Ashpole's very interesting and exact measurements of the absorption of viscose at high relative humidities.

Mr. S. Baxter (*Wrexham*) (*communicated*) : Bartell, Purcell and Dodd do not appear to be familiar with the work done in this country on the water repellency of porous surfaces.[12] [13] They consider water-repellent textiles in terms of Wenzel's theory which is inapplicable in this particular case, as the water-air component of fabric-water interface is ignored. It is probably the higher value of this component in the case of cotton cloths, as compared with Nylon cloths, which gives the greater increase in apparent contact angle.

The definition of water repellency in terms of the solid-water contact angle is erroneous as porous structures can be highly water repellent for any finite contact angle.

The contact angles determined in these investigations are the apparent advancing contact angles for the yarns comprising the fabric and are in no way a measure of the efficiency of the water-repellency treatment, unless the yarn structure is identical for each fabric tested as appears to be roughly the case here. The methods adopted by these authors would break down completely if used for fabrics of widely different structure, as the value of the angle measured by them, θ^A_W, is more dependent on yarn structure than the water-repellency treatment given.

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[11] Katz, *Kolloidchem*, 1918, **9**, 106 (through Freundlich, *Colloid and Capillary Chemistry*, 1926, p. 677).

[12] Cassie and Baxter, *Trans. Faraday Soc.*, 1944, **40**, 546.

[13] Baxter and Cassie, *J. Text. Inst.*, 1945, **36**, T67.

The view that a tightly woven structure is necessary for good water repellency is exploded by the duck's feather which is both highly porous and highly water repellent. Also highly porous fabrics can be made which have good water-repellency characteristics.'[13]

Dr. G. S. Hartley (*Harston*) said: Arising out of the paper of Dr. Stamm, I would ask Dr. Barkas whether in the examination of permeation of a composite material where both vapour-phase and liquid-phase diffusion may contribute, the idea had ever been tried of replacing the contained air by, say, hydrogen. If this could be done without structural damage, the vapour-phase diffusion would be accelerated by a known amount while the condensed-phase diffusion would be unaffected directly, although affected indirectly by the redistribution of concentration produced by the vapour-phase acceleration. In this way, a means of assessing the relative contributions of the two processes might be available.

Dr. W. W. Barkas (*Princes Risborough*) said: In reply to Dr. Hartley, as far as I know, no experiments of the type Dr. Hartley suggests have been made, in which the air was replaced by another gas during drying. There would be no difficulty in doing this and it would be interesting to see whether the results could be used to differentiate between flow in the vapour and in the adsorbed states. We have measured the rate of flow of water vapour through wood at constant vapour pressure difference and varying surrounding air pressures, but it is doubtful whether such data can be used to calculate the relative rates unless the mechanism of flow of vapour and air through the complex void structure of wood is understood. This is at present far from being the case.

Mr. S. Baxter (*Wrexham*) (*communicated*): The method of assuming that the boundary layer of still air to be the same over the leather as over the gel as used by Robinson *et al.* is not to be recommended as the thickness of the boundary layer is very dependent on the nature of the surface. Values of the boundary layer thickness formed with a variety of textiles[14] under air conditions comparable with those used by Robinson, Topp and Beakbane are given in the Table.

Material used.	D Diffusion Coeff. through Fabric.	M Sur. Coeff.	D_A Diff. Coeff. through Air.	D_A/M Bound. Layer Thickness cm.
Proofed blanket ..	0·25	0·20	0·27	1·35
Proofed serge ..	0·12	0·42	0·27	0·64
Proofed gabardine..	0·067	0·39	0·27	0·69
Proofed overcoating	0·20	0·35	0·27	0·77

It is seen that the boundary layer thickness varies considerably with surface structure and the method of using a fixed value for all leathers may lead to serious error especially if the thickness of the leather samples used is comparable with the boundary layer thickness.

Dr. I. W. Wark (*Melbourne*) said: Dr. Barkas has referred to the fact that drops of water may sit on a solid surface even though when rubbed in they wet it readily. This is but the old difficulty that a system does not necessarily reach equilibrium when left to its own devices. Similar phenomena occur in flotation. Even though a submerged solid surface may be in such a condition that an air bubble can adhere to it, a bubble which presses on it does not necessarily effect immediate contact. There is in fact an induction period before true contact ensues, and Sutherland considers that the inefficiency of the process is largely dependent upon the finite nature of this induction period.

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[14] Baxter, *J. Text. Inst.*, 1946, 37, T39.

Might I take this opportunity to draw attention to the unsatisfactory state of affairs with respect to use of the terms hydrophobic, oleophobic and hydrophilic. This has arisen, I suspect, from the fact that in a capillary tube air will displace water if the contact angle exceeds 90° ; water will displace air if the contact angle is smaller than 90°. This capillary phenomenon has given to the angle of 90° a greater significance than it deserves in studies of wetting.

On paraffin wax, which is considered a very hydrophobic surface, the angle of contact is *ca.* 110°. The surface has affinity both for water and for air, and it would be accurate to say that it is more hydrophobic than hydrophilic. Where the contact angle is specified there is no confusion. However, many writers use the term hydrophilic to imply a contact angle of 0° and the term hydrophobic to imply a finite contact angle because this means that the surface may be water-repellent in the sense used by Cassie, or amenable to flotation in the way I have described in my earlier contribution to the discussion. We cannot have it both ways, and I would suggest that the term hydrophobic be reserved for surfaces at which the contact angle exceeds 90°. Where the angle is under 90° but exceeds zero, the surface might be described as predominantly (but not completely) hydrophilic. For 0° one might use the term, completely hydrophilic. So far as I know, there are no known cases where the contact angle equals 180° : if there were, we might speak of a completely hydrophobic surface.

Dr. W. W. Barkas (*Princes Risborough*) (*communicated*) : In reply to Dr Wark, I should say that " the water drop sitting on the solid surface " *has* reached equilibrium under the conditions then operative. If these conditions are changed by rubbing the water into the surface, then a new set of conditions has led to a new and different equilibrium. The conditions may, of course, be slowly changing with time, but, in that case, the drop will finally reach equilibrium even if " left to its own devices."

Dr. J. M. Preston (*Manchester*) said : Dr. Henry considers the diffusion of heat and moisture through moderately dry textile materials, but it may also be of interest to mention some observations which have been made on moist materials. It was observed that two large and distinct temperature waves travel through a moist textile material during drying processes.[15]

The temperature distributions at successive times through the mass of a textile material being heated from one side are shown diagrammatically in figure 2. At any point in the material, there is first a rise, then a fall and, finally, a second rise of temperature, as the two temperature waves travel successively from the hot side towards the cool one.

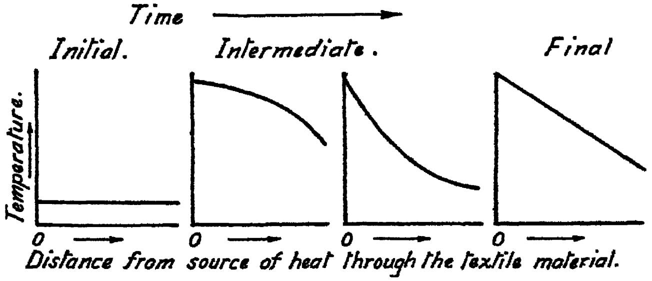

FIG. 2.

The first stage of this process is found to be associated with a marked migration of solute (if any is dissolved in the water present) in the direction of the source of heat. When the textile is quite moist and the drying is rapid, the migration of solute can be so marked as to remove it completely from those regions furthest from the source of heat. The phenomenon is observed equally, irrespective of the manner in which the heat is supplied, provided it is applied locally by conduction, convection or radiation, but is not observed when the heat for drying is supplied homogeneously by high frequency waves. The migration phenomenon has only been observed as yet when the moisture content exceeds the usual saturation values for water vapour. The phenomenon is not confined to water or to porous fibres. It is also seen when organic liquids and glass fibres are substituted for them.

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[15] Preston and Chen, *J. Soc. Dyers Col.*, 1948, 64, 60.

These and other considerations indicated that the first temperature wave we observed was caused by a cycle of distillation and condensation processes. In these, vapour moves away from, and liquid towards, the source of heat. The extraction produced by the latter part of the cycle causes the migration of solute towards the source of heat. As the material dries through the transfer of moisture away from the source of heat the distance the liquid has to travel lengthens, there is an increasing resistance to the maintenance of this cycle, and diffusive heat-transfer mechanisms on the lines of those discussed by Dr. Henry must operate alone. These require a greater temperature difference for a given rate of heat transfer. There is thus a fall of temperature as the heat is being removed on the cooler and damper side by an additional and easier mechanism. When finally the material dries throughout, the liquid-vapour heat-transfer mechanism previously operating on the cooler side of the material is eliminated and the temperature rises once more.

Dr. R. K. Schofield (*Harpenden*) said: The development of salt incrustations at the surface of saline soils is another example of the kind of behaviour described by Dr. Preston. I feel sure that Dr. Preston has given essentially the correct interpretation to his observations.

Mr. K. J. Nieuwenhuis (*Delft*) (*communicated*): The two equations for the penetration pressure of a liquid into a capillary, before and after the liquid surface has passed a constriction, which were given in Prof. Adam's paper, can be written as one equation, if the angles of inclination of the capillary walls are always measured clockwise from the normal on the general direction of flow of the liquid (i.e. the normal on the axis of rotation of the capillary) (Fig. 1 *a*, p. 8.)

Then $\varphi_1 = \varphi$
$\varphi_2 = (100° - \varphi)$
and φ varies between 0 and 180° before and after the liquid surface has passed the constriction.

$$p_i = \frac{2\gamma_L \sin(\theta_A + \varphi)}{r} \quad . \quad . \quad . \quad . \quad (c)$$

$$p_i > 0, \text{ when } \theta_A + \varphi < 180°$$
$$p_i < 0, \text{ when } \theta_A + \varphi > 180°$$
$$p_i = 0, \text{ when } \theta_A + \varphi = 180°$$

This means that when $0 < \theta_A < 90°$, the penetration pressure can be zero or negative, only *after* the liquid surface has passed the constriction. When $90° < \theta_A < 180°$, the penetration pressure can be zero or positive, only *before* passing the constriction.

The way in which p_i is influenced by θ_A is rather curious.

$$\frac{\delta p_i}{\delta \theta_A} = \frac{2\gamma_L \cos(\theta_A + \varphi)}{r}$$

Therefore, when $0 < \theta_A < 90°$, an *increase* in the value of θ_A means an *increase* in the (*positive*) value of the penetration pressure for values of φ, limited by

$$0 < \varphi < (90° - \theta_A)$$

and a decrease in the penetration pressure, when

$$(90° - \theta_A) < \varphi < 180°.$$

However, when $90° < \theta_A < 180°$,

an *increase* in the value of θ_A means an *increase* in the (negative) value of the penetration pressure (which therefore becomes *less strongly negative*), for values of φ, limited by

$$(270° - \theta_A) < \varphi < 180°,$$

and a decrease in the penetration pressure when

$$0 < \varphi < (270^\circ - \theta_A).$$

In order to investigate the influence of the value of γ_L on the value of p_t, we have to take into account that θ_A also depends on the value of γ_L. We can write

$$\cos \theta_A = \frac{\gamma_S - \gamma_{LS}}{\gamma_L}$$

because, strictly speaking, eqn. (*c*) is no longer valid when spreading occurs ($\gamma_L < \gamma_S - \gamma_{LS}$), as in that case $\cos \theta_A$ and $\sin \theta_A$ do not have any mathematical meaning, and θ_A has no physical meaning at all.

Therefore $$p_t = \frac{2}{r}\left\{\cos \varphi\sqrt{\gamma_L^2 - (\gamma_S - \gamma_{LS})^2} + \sin \varphi(\gamma_S - \gamma_{LS})\right\},$$

and $$\frac{\delta p_t}{\delta \gamma_L} = \frac{2\,\gamma_L \cos \varphi}{r\sqrt{\gamma_L^2 - (\gamma_S - \gamma_{LS})^2}}.$$

A decrease in the surface tension of the liquid always involves a decrease in the penetration pressure before the liquid surface has passed the constriction ($0 < \varphi < 90^\circ$); it always means an increase of the penetration pressure, after the liquid has passed the constriction ($90^\circ < \varphi < 180^\circ$). These are exactly the results one should expect also from a qualitative point of view. Before the liquid surface has passed the constriction, the free surface area of the liquid decreases as the liquid flows on; after having passed the constriction, the free surface area of the liquid has to increase again. It should be noted also that with capillaries of constant bore ($\varphi = 90^\circ$) the penetration pressure is completely independent of the surface tension of the liquid, in this case, where $\gamma_L + \gamma_{LS} > \gamma_S$, quite in accordance with eqn. (*b*).*

The above calculations have some importance with regard to the penetration of solutions of surface active compounds into porous materials (e.g. textiles). On penetration, the solution is exhausted, as the surface-active compound is adsorbed on the walls of the capillary. Before the liquid surface passes the constriction this exhaustion is counteracted by the fact that the free surface area of the liquid decreases. After the liquid surface has passed the constriction, the surface tension of the liquid will rise, not only because of the increase in the solid-liquid interfacial area, but also because of the increase in the free surface area of the liquid as the liquid flows on.

Therefore the *rate of diffusion* of the surface-active substance to the "penetration front" (the foremost layers of the penetrating liquid within the capillary) will have great influence on the surface and interfacial free energies, and consequently on the actual value of the penetration pressure too.

In his paper Dr. Robinson gives experimental evidence that Poiseuille's law holds even for the penetration of water into the very fine interstices of leather, which are presumably much smaller than in any artificially woven material. Combination of Poiseuille's law and eqn. (*b*) for the penetration pressure of a liquid into a cylindrical capillary gives for the length, l, of that part of the capillary which has been filled with liquid after t sec., if the liquid has not spread over the capillary walls before the capillary is being filled with liquid:

$$l = \sqrt{\frac{(2\gamma_S - 2\gamma_{LS} - Pr)\,rt}{2\eta}} \quad . \quad . \quad . \quad . \quad (d)$$

and, if the speed of spreading of the liquid over the capillary walls is greater than the speed of filling of the capillary:

$$l = \sqrt{\frac{(2\gamma_L - Pr)\,rt}{2\eta}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (e)$$

where η = the viscosity of the liquid *within the capillary*
and r = mean radius of the capillary over the length l.

In the derivation of these equations it is assumed that on the average the capillary can be regarded as a cylindrical capillary with a constant bore of radius r, over part of its length l. P here is the excess pressure of the air within the capillary, caused by the fact, that in general the air cannot escape freely from the capillary (e.g. with textile materials surrounded on all sides by water).

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* This Discussion, p. 104.

The linear rate of penetration $\frac{\mathrm{d}l}{\mathrm{d}t}$ decreases with decreasing value of the mean radius r, when $P < \frac{\gamma_S - \gamma_{LS}}{r}$ (no spreading occurs before penetration) or $P < \frac{\gamma_L}{r}$ (spreading has occurred before the penetration). When $P > \frac{\gamma_S - \gamma_{LS}}{r}$, or $P > \frac{\gamma_L}{r}$, the reverse is true.

The penetration comes to a standstill before or after the liquid surface has passed a constriction, when

$$\varphi \geqslant 180° - \theta_A,$$

because then the penetration pressure is zero or negative. Such a standstill can be overcome to some extent by mechanical agitation of the liquid, of the porous material, or of both, and especially by the differential pressures, set up by the "pumping action" of the falling-down of the materials in a normal washing machine with a cage rotating round a horizontal axis.

The requirements for very efficient wetting-out of a porous material by a solution of a surface-active (or rather, an interfacially-active) compound are:

(i) θ_A should be small, in order that the penetration pressure will not become zero or negative in the neighbourhood of a constriction. Probably, this is the reason of the fact, mentioned during the Discussion by Dr. Cassie, that for efficient penetration of water into a woven textile material the advancing contact angle should differ as little as possible from zero *;

(ii) this low value of θ_A should be caused by a low value of γ_{LS}, the free interfacial energy at the liquid-solid interface, rather than by a low value of γ_L, the surface tension of the liquid (cp. eqn. (*d*) and (*e*));

(iii) the viscosity of the liquid as it is present in the capillary, should be small, and at any rate the solute adsorbed on to the capillary walls should not clog the pores at all;

(iv) the rate of diffusion of the surface-active compound from the liquid in bulk into the capillary to the "penetration front" should be high.

Dr. J. Powney [16] found that addition of an alkaline or neutral salt to a solution of soap or a synthetic detergent of the long-chain sulphated type, impairs the rate of wetting, in spite of the fact that with soap solutions the interfacial tension at the solution-mineral oil (or xylene) interface is decreased by the addition of an alkaline salt (up to a certain *p*H value). In the Experimental Station for Laundering in Delft we have been able to confirm this salt effect under practical laundering conditions with soiled household linens. It is almost certain that this decrease in wetting efficiency by the addition of salt is caused by an important decrease of the rate of diffusion of the surface-active substance and by an increase of the viscosity of the solution.

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[16] Powney, *Wetting and Detergency* (London 1937), p. 185.

* This Discussion, p. 239.

V. DISCUSSION ON OLEOPHOBIC SURFACES

Dr. J. H. Schulman (*Cambridge*) (*communicated*): It has been described that built-up multilayers of certain soaps are hydrophobic and oleophobic [1] [2] and it has been known that calcium and barium soaps are not wettable by hydrocarbons. Recently [3] it has been shown that a monolayer of a long-chain hydrocarbon, when adsorbed onto a metal plate such as platinum by means of a polar group at one end of the molecule, for example an amine or alcohol, makes the metal plate, which is readily wettable by the hydrocarbon, oleophobic. The contact angle, which varies with the number and packing of carbon atoms in the film-forming material, and the nature of the oil, has a maximum value under these conditions of about 45°. The above results are obtained by adsorption or deposition of a monolayer or multilayers on a solid base. A very interesting example of this phenomenon not necessitating a solid base is given by hydrocarbons, like benzene, into which aluminium soaps have been dispersed. The resultant dispersion jellifies the hydrocarbon and makes the system oleophobic to the hydrocarbon. These jellies flow slowly under their own weight and consequently give a completely smooth surface in comparison with metal surfaces which have been polished or deposited on glass by evaporation of the metal.

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[1] Schulman, *Ann. Reports*, 1939, **36**, 109.

[2] Langmuir, Blodgett, Schaeffer, *J. Franklin Inst.*, 1943, **218**, 143.

[3] Bigelow, Pickett, Zisman, *J. Colloid Sci.*, 1946, **1**, 513.

Gelled hydrocarbons, with as little as 5 % of an aluminium soap formed *in situ* in the hydrocarbon, such as benzene, by means of a solution of an aluminium alcoholate to which two moles of a fatty acid and one mole of water have been added per aluminium atom, are oleophobic to benzene.[4] It would appear that a two-dimensional lattice of closely packed CH_3 groups, obtained by an interlocking of the polar groups at the other end of a straight hydrocarbon chain, is necessary to obtain an oleophobic surface. The inter-association of the polar groups can be obtained in the first case on the metal base by adsorbing polar groups which co-ordinate with the metal, or in the second case by a two-dimensional lattice of polar groups held together by hydroxyl bonding on the surface of the hydrocarbon. The theory and results of the second case are being published elsewhere.

Prof. N. K. Adam (*Southampton*) *said*: "Oleophobic" surfaces have been occasionally reported and also mentioned in this Discussion; "oleophobic" surfaces usually have a very high contact angle with water, indicating that the exterior surface consists of hydrocarbon groups, presumably mainly methyl groups at the extreme outside. If there is a contact angle with paraffin oil, the adhesion of the liquid paraffin to the solid paraffin-like surface must be less than that of liquid paraffin to itself; an angle of 90° would indicate that the adhesion of liquid to solid is half that of liquid to liquid. That would, if the "oleophobic" property is genuine, indicate a considerable, and to my mind very surprising, difference in chemical properties between liquid and solid paraffin-like surfaces. The contact angle, of the order 110°, between water and solid paraffin wax is equivalent to an adhesion about 45 ergs/sq. cm., *nearly the same as that between water and liquid paraffins.* Why should a solid, paraffin-like surface adhere to water as if it was very similar to a liquid paraffin surface, but to liquid oils as if it had many fewer groups per sq. cm. attracting the liquid ?

Dr. G. S. Hartley (*Harston*) said : In the case where the hydrocarbon chains are close-packed and all of the same length the outer surface consists of methyl groups. When there is irregularity it consists partly of methylene groups. Is it possible that the observed behaviour is due to a difference between "methyl liquid" and "methylene liquid"? The behaviour of the surface layers towards triptane (2 : 2 : 3-trimethyl butane) might be instructive.

Dr. D. J. Crisp (*Cambridge*) said : If γ_0^S and γ_0^L are the tensions of solid and liquid hydrocarbon surfaces, and are nearly equal as suggested by Prof. Adam from the similarity of their adhesional work to water, it requires only that the interfacial tension of the boundary—if it existed—should be greater than $\gamma_0^S - \gamma_0^L$ to prevent spreading. In other words, if γ_0^S is only slightly more than γ_0^L or less than γ_0^L, a finite contact angle would be expected, though it may be small.

It is easy to imagine that two similar kinds of molecule should spread over one another just because one expects them to be inter-miscible. In fact, however, if they are not miscible but have a finite interfacial tension, and if $\gamma_0 = \gamma_0'$ then neither spreads over the other, and both offer finite angles of contact.

There seems to me therefore no reason why the contact angle between a liquid and a solid paraffin should not be finite—if it were possible to observe it. Normally an oil is miscible with a solid hydrocarbon; it dissolves or soaks into the block. Only when one hydrocarbon surface is " anchored " by polar groups is it possible to observe a stable angle of contact between two hydrocarbon surfaces.

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[4] McRoberts and Schulman, *Nature* (in press).

It is well known that a drop of benzene or hexane stands with a finite angle of contact against a compressed film of stearic acid. This appears to me to be almost analogous to the systems of oleophobic coatings of metal soaps on metal surfaces described by Bigelow *et al.*[5] The tension of the paraffin-like monolayer, γ_0^s, is in both cases reduced until it prevents the oil spreading on it; in the case of the water monolayer this is achieved by externally applied surface pressure, at the metal surface by strong adsorption of the polar groups to metal. A perhaps stricter analogy would be the " oleophobic " surface of a saturated aqueous solution of lauric acid, for here the monolayer tension is also reduced by adsorption.

The essential points seem to be:

(i) the surface tension of a hydrocarbon-covered surface may be considerably modified by the degree of packing of the chains;

(ii) only a small decrease in tension of the paraffin-like surface is needed to produce a finite angle of contact with liquid hydrocarbon.

Prof. N. K. Adam (*Southampton*) said: I feel sure that, when a drop of benzene is placed on top of a monolayer of, say, a fatty acid on a water surface, it does not sit on top of the monolayer, but goes right through it to the water. It may either dissolve that part of the monolayer on which it is placed, or shove the monolayer aside. If the monolayer is confined by barriers so that the surface pressure is greater than the spreading pressure of the benzene, of course the benzene shows a contact angle; in other words, the surface tension of the water is so much lowered by the film that it is less than the sum of the surface tension of the benzene, and the interfacial tension of the benzene-water interface.

I wonder how many of the supposed cases of "oleophobic" surfaces could be explained by the oil dissolving away, locally, one or more top layers of molecules, being then laterally compressed by the surface pressure of those parts of the top layers which, being outside the periphery of the oil drop, are not dissolved by it? It would seem easy for an oil drop to penetrate right through a thin coating of wax, and come into contact with any underlying hydrophilic layers; and very probably an oil drop in such a position would show a considerable contact angle with the surface. The original surface could scarcely be properly called an " oleophobic surface," in such a case.

Dr. D. J. Crisp (*Cambridge*) said: I agree that if the monolayer at the oil-water or oil-metal interface is dissolved away the interfacial tension will be raised and the contact angle will increase. I do not, however, think it is always necessary to postulate this, though the orientation and packing of the monolayer will be changed by the presence of an oil instead of air or vapour above it.

For instance, a monolayer of oleic acid at 32 dynes surface pressure is " oleophobic " to oleic acid droplets, but there can be no doubt that an orientated monolayer exists both between water and air and between water and liquid oleic acid.

Dr. C. Kemball (*Cambridge*) said: There is an interesting piece of evidence in support of Dr. Hartley's suggestion that the interaction between two surfaces mainly composed of methylene groups may differ from that between a surface of methylene groups and one of methyl groups. The van der Waals' interaction between such non-polar surfaces will depend not only on the polarisability of the groups but on their geometry. This is shown strikingly by the difference in the heats of adsorption of benzene and cyclohexane on mercury. The values are 16·1 and 12–13 kcal./mole respectively. The polarisabilities are $10{\cdot}3 \times 10^{-24}$ and $10{\cdot}9 \times 10^{-24}$ cc., which means that the difference in the heats of adsorption must be connected with the different spacial arrangement of the two substances or, in other words, the " availability of the polarisability " for adsorption on a plane surface. Considerations of this sort will undoubtedly apply to surfaces of methyl groups and the normal surface of a liquid hydrocarbon which presumably contains a greater proportion of methylene groups.

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[5] Bigelow, Pickett and Zisman, *J. Colloid Sci.*, 1946, 1, 513.

Dr. M. Joly (*Paris*) said: Wetting or spreading can be compared with a superficial solubility and then these phenomena depend on the compatibility of the structures. By this means it is possible to understand what happens in the case of the oleophobic films mentioned by Dr. Schulman and to see why a non-polar oil does not spread on the surface of a solid paraffin wax.

The surface of a solid paraffin is formed by CH_3 groups arranged in a rigid four-angled centred lattice and the smallest distance between two neighbouring CH_3 groups is about 4·4A. On the other hand, the surface of a liquid paraffin is built up of CH_3 groups arranged in a quasi-hexagonal lattice, the mean distance between two neighbouring CH_3 groups being about 4·5A. This quasi-lattice is deformable but in a small range only. From the great difference between these two lattices it results that superposition of both structures is impossible and hence that the oil does not wet the solid paraffin wax. For spreading, it is necessary to introduce some disorder into the solid lattice; the corresponding CH_3 groups are then capable of some mobility and the structures of the two systems in contact become compatible, superficial solubility occurs and the paraffin oil wets the paraffin wax.

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A GENERAL DISCUSSION

ON

THE PHYSICAL CHEMISTRY OF PROCESS METALLURGY

GENERAL INTRODUCTION

A GENERAL DISCUSSION on the Physical Chemistry of Process Metallurgy was held at Ashorne Hill, nr. Leamington Spa, Warwickshire (by courtesy of the British Iron and Steel Federation) from 23rd September to 25th September, 1948. At the opening and closing sessions the Chair was taken by the President, Prof. A. J. Allmand, F.R.S., and during the remainder of the Meeting by Sir Andrew McCance, F.R.S. About 130 members and guests were present; among the distinguished overseas guests, the President welcomed the following :—

> Mr. Howard Biers (New York), Prof. J. Chipman (Cambridge, Mass.), Mr. C. Danielsson (Domnarvet, Sweden), Mr. M. N. Dastur (Cambridge, Mass.), Prof. R. Dürrer (Gerlafingen, Switzerland), Mr. J. D. Fast (Eindhoven), Mr. and Mrs. Sven Fornander and Master Henrik Fornander (Surahammar, Sweden), Dr. F. C. Frary (New Kensington, Pa.), Dr. W. Gaade (Amsterdam), Dr. and Mrs. J. Görrissen (Oslo), Dr. C. H. Herty (Bethlehem, U.S.A.), Monsieur Husson (Saint-Germain-Laye), Prof. Bo Kalling (Domnarvet, Sweden), Monsieur H. Malcor (Saint-Germain-Laye), Dr. M. Pourbaix (Brussels), Prof. M. Rey (Paris), Monsieur Rocquet (Saint-Germain-Laye), Madame C. Rorive-Bouté (Brussels), Prof. E. Rudberg (Stockholm), Prof. P. van Rysselberghe (Oregon), Mr. G. Szasz (U.S. Embassy, London), Dr. M. Tigerschiöld (Stockholm), Mr. and Mrs. A. Wahlberg (Bofors), Prof. M. Wiberg (Stockholm), Mr. and Mrs. S. H. Willners (Trollhaettan).

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THE PHYSICAL CHEMISTRY OF PROCESS METALLURGY

INTRODUCTORY ADDRESS

SIR ANDREW McCANCE

Received 23rd September, 1948

As one who took an active part in the first General Discussions on the Physical Chemistry of Steelmaking which the Society held in 1925, it is a matter of particular pleasure to me to be present at this Discussion called together for the purpose of stating and discussing the present state of our knowledge of this important subject.

The interest of this meeting is further emphasised by the contributions of so many workers in this field from other countries and to whom we extend a specially cordial welcome.

When the papers to be presented at the sessions now starting are compared with those read at the meeting 23 years ago, there is one marked difference which is noticed immediately. The difference I see is that the ideas put forward now are supported by a wealth of experimental results whereas the earlier papers were rich in unconfirmed theoretical deductions. There is no doubt, however, that the stimulation given to the study of this subject by that meeting was encouraged by this very fact, for it impelled those who disagreed with the conclusions to seek support for their views by experimental methods.

That the first general discussion did give an immense stimulus to the study of the physical chemistry of steelmaking is a fact which is acknowledged gratefully by all metallurgists. I am certain in the wider field which it covers this meeting will also be equally effective.

The application of the principles of physical chemistry to metallurgical processes appeals to us for two reasons. It appeals to those of us who are interested in the development of the theory of high-temperature processes at high concentrations in which our knowledge is still in a somewhat crude and elementary state, and it appeals to those in the metallurgical industries who seek from it a better and more quantitative control over the production processes in their charge.

From the latter angle I can speak from my own experience in the steel industry. The developments in the open-hearth process during the last 20 years have largely, if not wholly, arisen from the physico-chemical approach to the open-hearth reactions—an approach which has now become the universal practice of all those engaged in this branch of steel manufacture. But we are still far from exercising that exact quantitative control which must be the ultimate aim. Even in the simplest reactions like the reduction of ferrous oxide by carbon the values of the equilibrium constant obtained in the laboratory and in the melting shop still differ appreciably and it cannot be said with certainty why this should be so.

With other reactions the position is even worse, for even under laboratory conditions there is the disappointment of finding that equilibrium constants cannot be made to remain constant without the help of the most empirical adjustments. There are, for instance, the reactions which control the removal of phosphorus by a basic slag where this difficulty, which raises important questions, is particularly noticeable. In these complex slags, is it perhaps wrong to expect a constant relation between the different reacting constituents regarded as molecular entities when they exist in the liquid state probably as atomic, or perhaps even as ionic, mixtures ?

This thought is strengthened by the success which has attended the consideration of phosphate glasses as ionic mixtures where it has been found for instance that the density can be expressed accurately by a formula of the type $V = \frac{V_0}{1 - aR}$ where a is a constant and R is the ratio of the proportion of divalent oxygen ions to that of the basic ions present. The conductivity variation with temperature of many such glasses is very similar to that of open-hearth slags and there are other points of similarity so that this method of approach is worth exploring.

It will be recalled that a paper was read before the Faraday Society in 1938 by Herasymenko drawing attention to the possibility of regarding steelmaking slags as ionic solutions although his ideas at that time were still dominated by the conception of molecular groups within the fluid slag.

Nevertheless, before conceding that a new development in outlook is necessary we must assure ourselves that the present theories used to interpret experimental results are sufficiently exact for the purpose and at the present time this is unfortunately just what cannot be done.

The fundamental basis of the application of theory to metallurgical reactions is the equation—

$$\frac{\mathrm{d}}{\mathrm{d}(1/T)} \log K = E + \int C_v \mathrm{d}T$$

which is full of difficulties in spite of its apparent simplicity. Its successful use depends on two assumptions—(1) that the energy of reaction E is known over the whole range of concentration of the reactants, and (2) that the specific heats are also known and known in a form that permits of integration. We all know how very far this is from being true.

Ignorance forces us to assume that both factors are constant—and it is astonishing to realise how very often this happens to be so nearly true in high-temperature chemistry. The next stage has been to substitute a variation like $a + bT$, or $a + bT^2$, and to obtain the coefficients a and b from other known data, or with greater accuracy to express the variations by a more extended expansion in terms of the temperature. These methods are essentially empirical and the results cannot be used outside the range of temperatures for which the experimental data were already available. It was for this reason that the first attempts to calculate the equilibrium constants at high temperatures from information obtained at much lower temperatures failed to give accurate information. Nor is the position to-day in this respect much better than it was 20 years ago.

On the cognate problem of determining the variation of interaction energy with concentration an adequate solution is still awaited in spite of the vast amount of work already carried out on the subject. This, however, may not be altogether surprising when it is remembered that even in the case of the simplest ionic electrolytes a complete solution of the energy equation has not yet been worked out.

The approach by means of activities or activity coefficients is, of course, identical in principle with the approach from the energy standpoint and in some ways it is more easily applied, but it relies on applying the deductions from one set of experimental data to another set and it cannot be used with any confidence outside the limits of the known data.

The questions are fundamental and if we feel as metallurgists that in the application of physical chemistry to metallurgical reactions our theoretical foundations are not very secure, let us console ourselves with the thought that all physical chemists are in exactly the same position as ourselves. And it may well be that the desired theoretical advances will arise out of the study of the high-temperature reactions which are of such particular interest to this meeting.

In closing could I make one special plea on behalf of all the metallurgists interested in this subject and perhaps even on behalf of others as well. That plea is for the acceptance of an agreed set of symbols and meanings for the commoner terms used by physical chemists. What some authors call " thermodynamic potential " is called " chemical potential " by others, and the terms " free energy " and " available energy " are sometimes applied indiscriminately. One has only to read the papers before this conference to find that there is not yet full agreement in the symbols to be used for representing the more frequently used terms. A joint committee of the scientific societies concerned made agreed recommendations on this matter in 1937. It would be very helpful if steps could be taken to put the committee's findings into consistent use.

PHYSICO-CHEMICAL PRINCIPLES IN PROCESS METALLURGY

By Sir Charles F. Goodeve

Received 26th July, 1948

Part I. Introduction

The term " physical chemistry " covers a rather ill-defined branch of science but is generally interpreted as the application of physical principles to chemical reactions. Some of these principles have been borrowed from physics, others have been developed primarily in their relations with chemistry, that is, by physical chemists. The object of this paper is briefly to set out, for those not acquainted with this branch, some of the more important of these principles in a way that will show their application to the types of chemical reaction which are the concern of this Discussion. There are two important approaches in physical chemistry, the kinetic and the thermodynamic approaches, and, although each of these is independent of the other, they have many points of contact. Before discussing these, we will examine the nature of the substances in which we are interested.

The Gaseous, Solid and Liquid States

Many metallurgical reactions involve gases at high temperatures and at moderate pressures, conditions under which it can be assumed that the ideal gas law, $pv = nRT$, applies with an accuracy far better than that required to match any existing quantitative measurements. These gases are commonly derived from air by combustion and may contain N_2, CO_2, H_2, H_2O, CO and O_2, etc. The thermodynamic approach is based on the partial pressure of each of the components of a gas.

Metallurgical reactions also involve ores containing compounds of a metal with a non-metal, oxygen, sulphur, silicon, etc. We know a great deal about the arrangements of the atoms and about the spacings and the forces between the atoms for many of the pure compounds in the solid state. We also have extensive thermodynamic data, heats of formation, specific heats, etc., but much more is needed. Most ores are complex mixtures of compounds and indeed the compounds themselves often exist over a range of composition lying about that of the chemical formula. FeS, for example, has a wide range, ZnO a narrow.

Metals behave as if they consisted of agglomerates of positively charged ions bound together by a " fluid " of electrons, the whole, of course, being electrically neutral. The ions consist of the metal nuclei plus all their " inner " electrons, that is, all the electrons in completed rings. The binding power of the remaining or conducting electrons arises from the fact that they are free to move throughout the mass of metal and, in accordance with wave-mechanical principles, are able on the average to spend more of their time closer to the positively charged ions than they would if they formed the electronic systems of separate neutral atoms in free space. This means that there is a net lowering of potential energy when the vapour of a metal condenses, this lowering exhibiting itself by the evolution of the latent heat. This also means that there is little left here of the concept of valency, each atom or ion of the metal being bound equally to the eight or twelve atoms which usually surround it. Some authors,[1] however, prefer to retain the idea of valency bonds with modifications based on resonance between bonds.

Liquid metals, the more common product of reduction reactions, are similar to the solid except that each ion spends most—or at least a large part—of its time other than in its " crystal position " in respect of its neighbours.

It is not surprising, therefore, that solid—and more particularly liquid—metals are good solvents for any species that can give up one or more electrons. Thus atomic hydrogen or nitrogen is soluble in most metals while inert gases and molecules, such as H_2 and N_2, are insoluble. Metals themselves have a considerable mutual solubility and indeed it is generally possible to realise experimentally a temperature above which any particular pair of metals is mutually soluble in all proportions. This high mutual solubility in the liquid state, limited only by the size effect (e.g., lead atoms do not readily go into melts of smaller metal atoms) sets a difficult problem to the refiner of metals.

Part II. Molecular Kinetics

The kinetic approach starts with a mental picture of the intimate molecular mechanism of a chemical change and follows with mathematical deductions to allow comparison with results of experiments. Whilst this approach has had its greatest success in application to gaseous reactions, there is no doubt that certain of its principles are of general application The reactions most carefully studied include that of hydrogen and iodine to form hydrogen iodide, and the reverse reaction. For illustration it is proposed here to take a reaction not studied kinetically but one which is more familiar to process metallurgists, the reduction of zinc oxide vapour by carbon monoxide. This reaction probably takes place to a small extent in the preparation of zinc despite the fact that the vapour in equilibrium with solid ZnO consists principally of the Zn and O_2.[1a]

In a free molecule of ZnO the oxygen atom is held to the zinc atom with a bond strength such that it would require about 100 kcal /g. mol. completely to separate them.[2] When this pair of atoms is pulled apart from the minimum value at about 2 A. and thus against the force of attraction, the potential energy rises according to curve I in Fig. 1. Conversely, an oxygen atom in free space in combining with a Zn atom will " roll down " this potential energy curve until it meets the repulsion force at a close distance. The ordinary molecules of ZnO will contain varying amounts of vibrational energy and this is pictured on the diagram as an oscillation of the oxygen relative to the zinc between a position say at *b* and a position *b'*. The potential energy follows the dip of the curve while the kinetic energy rises and falls to conform to the constancy of the sum, the total vibrational energy.

Similarly, if an oxygen atom approaches a CO molecule on the carbon side, a valency bond to produce CO_2 is formed with an energy of 127 kcal./g. mol., curve II. (The diagram is complicated by the fact that CO must change its electronic state before it can exhibit a valence force for oxygen.)

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[1] e.g., Pauling, *The Nature of the Chemical Bond* (Cornell University Press, 1940).

[1a] Pourbaix and Rorive-Bouté, This Discussion.

[2] This value is deduced by comparison with values for similar molecules ZnS, SnO, BaO, etc. It is in harmony with thermochemical data plus an estimate of the heat of vaporisation of ZnO. Division of the values by Avogadro's number, $6\cdot023 \times 10^{23}$, gives the energy per pair of atoms.

The reaction between ZnO and CO *might* be able to take place by a mechanism in which the O atom first separates from the Zn atom and later collides and combines with a CO molecule. Before the oxygen could separate, the molecule would have to gain at least 100 kcal /g. mol. of vibrational energy and we will see later that this is a very improbable occurrence. Much the easier course for this reaction is during a collision between a ZnO and a CO molecule. To give a complete picture, three-dimensional curves are required,[3] but an outline picture is given in Fig. 1. Molecules have a certain size (related to the volume they occupy in the solid state) and large forces or energies of repulsion arise if an attempt is made to bring them closer together than this size normally allows. When two molecules collide with a kinetic energy of, say, 25 kcal./g. mol., the potential energy of the whole system Zn — O — C = O rises to this value before the parts are brought to rest. This is shown in Fig 1 by the elevation of the

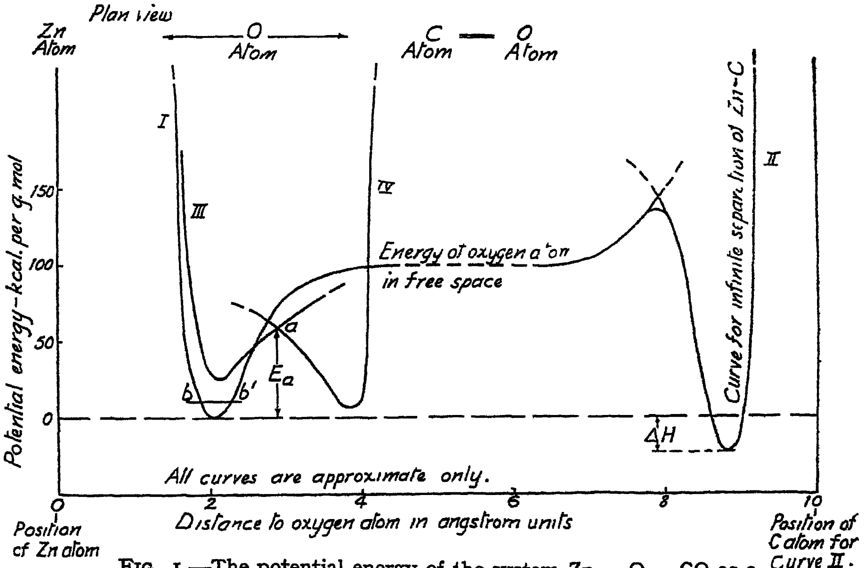

FIG. 1.—The potential energy of the system Zn — O — CO as a function of the movement of the O atom from the Zn to the CO.

curves I and II to the positions III and IV respectively when the closeness of approach is such that the Zn — C distance is 5 A. (It is assumed that the atoms are in a line as shown in the plan view.) However, the curves have become broader due to the weakening of the chemical bonds and now overlap at a point *a* considerably below the 100 kcal /g. mol. energy level of the free oxygen atom. Closer approach will not alter the position of *a* very much because the curves themselves rise rather rapidly for closer distances. The height of the lowest point of this energy barrier is known as the energy of activation E_a. The value suggested by Fig. 1 is 60 kcal./g. mol. above the original energy of ZnO + CO in free space.

Our picture of the course of this reaction can now be completed. Two molecules with a total energy between them in excess of E_a collide with favourable orientation and arrive at the position of the activated complex illustrated by curves III and IV. The total energy of this system swings through the whole complex and at some phase becomes concentrated in the Zn — O bond. The oxygen atom separates to the point corresponding to *a* and passes over into combination with the carbon.

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[3] Eyring and Polanyi, *Z. physik. Chem. B*, 1931, **12**, 279. Goodeve, *Trans. Faraday Soc.*, 1934, **30**, 60.

If all the information existed here as it exists in the case of the hydrogen and iodine system, it would be possible to test this picture against experimental observations. The reaction velocity could be predicted from the equation.[4]

$$\text{Molecules reacting per second} = PZe^{-E_a/RT} \quad . \quad . \quad (1)$$

where Z is the number of collisions between reactive molecules per second and P, the steric factor, the fraction of these collisions that are favourably oriented. The term $e^{-E_a/RT}$ is (approximately) the fraction of the collisions which have an impact energy greater than E_a and is derived from the Boltzmann distribution of energy in a system of molecules. The value of E_a can be determined independently from the temperature coefficient of the reaction velocity and the value of Z from the diameter of the molecules and their mean velocities. The value of P can only be deduced approximately and for the above reaction is not likely to be much below unity.

The reverse reaction, the attack of Zn on CO_2, can also be pictured from Fig. 1. The initial position of the oxygen atom would be at the bottom of curve II and the system would require energy E_a' to bring it to the point *a* before the atom could pass over to form ZnO. The value of E_a' is related to that of the forward reaction by the equation :

$$E_a' - E_a = -\Delta H, \text{ the heat evolved in the reaction.}$$

Liquid Systems

Eqn. (1) has been found to be generally applicable to reactions in liquids.[5] The value of Z is found to be effectively the same as it would be in a gas in the cases in which solvation effects are not predominant and the reacting molecules are simple. At first sight this may appear surprising because the net movement of a molecule in a liquid is much slower than in a gas, despite the fact that its average velocity is the same, because it performs a number of oscillations (on the average N_d) in any one position before moving to the next. However, the loss from this effect is compensated by the fact that, when this molecule does arrive alongside a molecule with which it might react, it makes N_r oscillations or collisions with that molecule rather than the single collision that it would have made if it were in a gas. N_r is normally exactly equal to N_d and as they come into eqn. (1) in the numerator and denominator respectively, they cancel out. Although we have not much experimental evidence to aid us, it seems reasonable to assume that, in molten metals and to a less extent in molten slags, atoms or simple molecules behave as in other simple solutions and the collision frequency Z is approximately the same as it would be if they were at an equal concentration in the gaseous phase.

The meaning of a collision in the liquid state requires, however, closer examination. An important reaction in many metallurgical processes is that between carbon and oxygen atoms " dissolved " in a metal liquid. These atoms lie in the spaces or interstices left between the larger metal atoms and are best considered as not combined with any particular neighbours but rather with all of them. They are able, however, to jump (diffuse) from one empty space to another with only a small energy barrier to be overcome, and indeed carbon has been found[6] to move towards the cathode when an electric current is passed through γ-iron containing carbon. There will be a greater energy barrier protecting a space already occupied by another atom but if this atom is one capable of forming a chemical bond with the incoming atom, as in the case of carbon and oxygen, the energy of activation is likely to be low. (This can be deduced if the potential energy curves are drawn corresponding to those shown in Fig. 1.) It seems best, therefore, to consider a " collision " in such systems as an attempt by one atom or molecule to enter a space or interstice already occupied by another atom or molecule.

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[4] For full details see Hinshelwood, *The Kinetics of Chemical Change* (Clarendon Press, 1940), p. 51.

[5] See Moelwyn-Hughes, *The Kinetics of Reactions in Solution* (Clarendon Press, 1947), p. 68.

[6] Seith and Kubachewski, *Z. Elektrochem.*, 1935, **41**, 551.

The carbon monoxide molecules formed in this reaction may suffer dissociation again or join together to form a bubble of gas. Owing to the facts that this growth requires a rapid succession of collisions with fresh CO molecules and that a liquid metal will resist with great energy the formation of a hole large enough to form the nucleus of a gas bubble, this second stage of the reaction is likely to be slow. It is generally believed to be the controlling stage and might, indeed, only proceed on a surface. This is borne out by the observation that supersaturation of a liquid metal with CO is common.

In some contrast to the previous case of a reaction between two interstitial atoms, we have cases where one of the atoms forms part of the metal lattice or of the remnants of the lattice in the liquid, such as in the reaction between oxygen and aluminium. This metal is added in small quantities to liquid metals as a deoxidiser because of its high affinity for oxygen. The reaction is too fast to study but this is not surprising as no energy of activation is to be expected between two atoms or ions moving (substantially) freely through the solution and with no matter obstructing close contact. This means that the rate of the reaction will be equal simply to the rate of collision between Al and O, although in this case it is necessary to reduce the value of Z calculated from the gas value because N_r now equals unity and the compensating mechanism just described does not enter. A rough calculation shows that if one portion of molten iron containing 0·2 atomic % oxygen was instantaneously and perfectly mixed with another portion containing an equivalent amount of aluminium, the reaction should be complete in 10^{-8} sec.

Reactions in the Solid State

In contrast to reactions in the liquid and gaseous states, those in the solid are inevitably much slower. In some cases the collision frequency Z in eqn. (1) is much reduced ; N_d has become extremely large and N_r cannot keep up because a chemical reaction takes place first. This means that diffusion becomes the rate-determining step and a value of E_a obtained from a temperature coefficient would refer to the energy required to permit a jump of the diffusing species from one position to another. As a considerable number of such jumps must take place before a pair of reacting molecules or atoms become neighbours, only a very slow reaction is possible. In other cases, the value of E_a for the final reaction may be very large because more energy is required to make space for the products of the reaction. A good example is the reaction involved in the penetration of iron sulphide into iron.[7] As the temperature is lowered, this reaction suddenly becomes immeasurably slow at the eutectic point, i.e., where the liquid phase disappears.

Reactions between two solids, no matter how intimately they are mixed, are likely to be even slower. In the absence of a gaseous or liquid phase, diffusion can only occur via the points of contact between the particles. Very small traces of gas or of liquid are likely to produce a reaction which would mask any reaction truly in the solid phase. Experimental confirmation of these predictions has been obtained for ZnO reduction by carbon. Bodenstein [8] showed that this reaction proceeds entirely via the gaseous phase, carbon monoxide acting as a carrier, taking oxygen from the oxide and regenerating itself by the reaction of CO_2 with the carbon. Evidence is lacking regarding the iron oxide—carbon reaction ; many authors assume that this can proceed via the solid state but undoubtedly it goes much faster when liquid or gas phases are present.

Reactions on the Surfaces of Solids or Liquids

An intimate kinetic knowledge of a reaction between molecules in the gaseous or liquid state and molecules of a solid is difficult to obtain and few reactions have yielded to study. In most of the many reactions studied, little information is available as to the nature of the surface and as to the immediate energetic nature of the product. The surface layer may differ from the bulk immediately the reaction has started, if not before, and most surfaces are at least partly covered by an adsorbed layer. However, we can say with a good deal of confidence that, if a molecule of CO collides with a clean surface of ZnO, the energy relations can be described by curves such as those in Fig. 1.

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[7] Preece and Irvine, *J. Iron Steel Inst.*, 1947, **157**, 336.

[8] Bodenstein, *Trans. Amer. Electrochem. Soc.*, 1927, **51**, 365.

Similarly, our picture of the reaction of two molecules across an interface between a liquid and a solid, or of one molecule crossing the interface, must be basically the same as the collision mechanism for a gas. Where both layers are fluid it is possible to make the simplifying assumption that the surface layer is essentially the same as the bulk, except for concentration gradients set up where the reaction rate at the interface exceeds the diffusion rate to the surface.

Collision Frequency and Energy of Activation

The calculation of the collision frequency and the determination of the energy of activation for a given reaction are both relatively easy, especially in the gaseous phase, and full descriptions of the methods are given in standard textbooks.[4] [5] It is generally insufficiently realised how great are the number of collisions. For example, at a partial pressure of 1/10 atm., 10^{23} molecules collide with every sq. cm. of surface per second. Molecules in a liquid are vibrating at about 10^{13} times per second and, at an interface, they each make approximately this number of attempts per second to cross the interface. There will be about 10^{15} molecules per sq. cm. and, if one in a hundred of these is of the species we are studying, this means 10^{26} collisions per cm.^{2} per second.

Homogeneous collision frequencies are even higher, 10^{30} or more bimolecular collisions per cm.^{3} per second being a common occurrence both in gases and liquids. As all of these values depend only on the square root of the absolute temperature, these orders of magnitude are the same throughout the range of temperature of interest here. Furthermore, the steric factor, P, can be ignored in these rough figures, as for simple molecules it usually lies between 1 and 10^{-1}.

The energy of activation is determined from the temperature coefficient of the reaction but is a realistic figure only if the course of the reaction is known. Values up to 100 kcal./g. mol. or higher are known in vaporisation reactions but such high values in ordinary chemical reactions are rare; the values for the reactions of interest to metallurgists lie usually between 25 and 75 kcal.

The approximate values of $e^{-E_a/RT}$ for a few values of E_a and of T are given in Table I.

TABLE I

Temp.			Energy of Activation				
° C.	° K.		25 kcal.	50 kcal.	75 kcal.	100 kcal.	
250	523		10^{-10}	10^{-21}	10^{-31}	10^{-42}	Immeasurably slow
500	773	Immeasurably fast	10^{-7}	10^{-14}	10^{-21}	10^{-28}	
750	1023		10^{-5}	10^{-11}	10^{-16}	10^{-21}	
1000	1273		10^{-4}	10^{-9}	10^{-13}	10^{-17}	
1500	1773		10^{-3}	10^{-6}	10^{-9}	10^{-12}	

The very important effect of this term, $e^{-E_a/RT}$, can be seen from this table; the selection of only those collisions between pairs of molecules with a critical amount of energy between them bring the frequency of successful collisions down to measurable limits. A reaction rate of 10^{13} molecules per cm.^{3} per second is just measurable and one of 10^{17} too fast to measure.

In practice, the ratio of surface to bulk varies widely but, if a system is chosen where 1 cm.^{3} exposes about 10 cm.^{2} of surface, the $e^{-E_a/RT}$ term would have to be of the order of 10^{-9} for gases and 10^{-12} for liquids to bring the reaction rate into the normal range. The band enclosing these is outlined in thick lines in Table I. It is seen, therefore, that an estimate can be made of the energy of activation from the temperature at which the reaction begins.[9]

Various other important generalisations can, however, be made. The first is that higher energies of activation would be necessary to bring a homogeneous reaction down into the measurable range than an interfacial reaction because of the greater frequency of bimolecular collisions. The second is that, at a temperature 250° above that at which a reaction starts, the rate should be about one thousand times faster. Often in metallurgical processes, this is not the case, and indeed the observed temperature coefficient and the derived value of E_a are often lower than is to be expected from the temperature at which a reaction starts. This is usually interpreted as meaning that the rate is largely controlled by the slowness of a diffusion process.

Diffusion

The phenomenon of diffusion is of such importance in process metallurgy that it would justify a separate Part of this paper. The subject is, however, a very extensive one and is well covered in several good text-books.[10] The elementary principles of diffusion are comparatively simple and well known, but the recent additions to our knowledge are extensive and difficult to summarise.

Some idea of the importance of diffusion may be gathered from the fact that a chemical reaction between oxygen in air and carbon dissolved in liquid iron takes much longer in the open-hearth furnace than in the Bessemer converter, where it proceeds as rapidly as the oxygen can be delivered to the metal. A strict comparison needs to take account, in the case of the open-hearth furnace, of the parallel reaction between iron ore and carbon. Nevertheless, a large part of the difference is due to the presence between the air-gas mixture and the iron of a blanket of slag which is necessary for other refining purposes.

If diffusion is recognised as the rate-determining process, then the reaction can generally be speeded up by agitation of the reactants or by increasing flow rates of gases, thus increasing the turbulence. In the open-hearth furnace the reaction itself stirs the bath by the CO evolved and thus accelerates the reaction, this self-accumulative effect sometimes throwing the whole system out of control. Phosphorus removal can be speeded up to take place in a few seconds by the violent agitation that occurs in the Perrin process. Diffusion and turbulence can sometimes be improved by lowering the viscosity; calcium fluoride is added to slags for this purpose.

Part III. The Thermodynamic Approach

While the kinetic approach gives a more intimate picture of the nature of a chemical reaction, it lacks the quantitative exactitude of the thermodynamic approach. The abstract nature of the latter, however, limits its usefulness but this abstract nature can be reduced if attention is first focused on the more simple chemical processes, the movement of any given element from one phase or one state of chemical combination to another. Indeed, process metallurgy is principally concerned with such chemical processes. Our first object will be to find a method of detecting a tendency for a movement to take place in a particular direction and to measure this tendency when it does exist.

It is not surprising that a major factor in determining the tendency to move is commonly the relative strengths of the total forces, chemical plus physical, in the two states, the element under consideration tending to move under the influence of the stronger force and thus to the position of lower potential energy. This manifests itself as an evolution of heat, the value of which for the ZnO–CC reaction being given by ΔH in Fig. 1. This factor is very nearly constant independent of temperature.

The second important factor in the tendency to move arises from the thermal agitation of the molecules and of the atoms in the molecules. All matter above the absolute zero has a tendency to move to the state of least restriction or order; a gas tends to expand to infinite space, a liquid to change to a gas, an ordered solid to change to a disordered liquid, a molecule to break up into atoms or ions, a set of molecules to change to another set incorporating a larger number of gaseous molecules, etc. This part of the tendency increases with thermal agitation, that is, with temperature.

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[9] See Hinshelwood, *loc. cit.*, p. 49.

[10] Barrer, *Diffusion in and through Solids* (Cambridge University Press, 1941). Also Glasstone, Laidler and Eyring, *The Theory of Rate Processes* (McGraw-Hill, 1941).

Other factors, such as pressure on condensed phases and electrical fields, are of importance in some branches of physical chemistry but are less frequently found in the processes considered in this Discussion.

The condition of equilibrium is obviously the condition where the net tendency is zero. This means that the two factors, the heat and the restriction factors, exactly compensate one another. For a liquid in equilibrium with its vapour, the tendency for the molecules to condense, measured by the latent heat of condensation, is exactly equal and opposite to the tendency to escape. The higher the temperature, the more active the tendency to escape.

Chemical Potential

This last statement indicates the answer to the problem of how to measure the net tendency. Let us first look at a parallel problem. We have seen that a piece of metal consists of a lattice of ions and a " fluid " of electrons. The number of these electrons, while being close to the number of positive ion charges, need not be exactly equal to it and two pieces of metal may differ in their departures from neutrality. In such a case, we say that these pieces of metal have a difference of electrical potential between them and if they are brought in contact, there will be a movement of electrons from that at the higher negative potential to the other.

The electric *potential difference* $\Delta\varphi$ is a measure of the *direction* and *intensity* of the tendency of electrons to move. It can be measured quantitatively by the work *obtained from* the system in the transfer of a unit amount of electricity from the metal at the higher potential to the other at the lower or by the work *done on* the system to transfer this amount of electricity in the reverse direction, i.e., " up-hill." If these are measured reversibly, that is, in the absence of friction, both works are equal and opposite and uniquely describe the intensity of the tendency. It is assumed, of course, that the test transfer does not affect the state of either of the pieces of metal, and in practice one thinks in terms of an infinitesimal amount of transfer, dn. Thus

$$\varphi_2 - \varphi_1 = \Delta\varphi = -\frac{dw}{dn} \quad . \quad . \quad . \quad (2)$$

If work is obtained in the transfer from state (1) to state (2), that is, dw is positive, then the second state is at the lower potential. (In practice, the term " voltage " is used and is defined as this work potential divided by the charge on the electron.)

As an alternative parallel problem we could have chosen two vessels containing liquid and in a gravitational field. The difference in gravitational potential is defined in the same way, i.e., by eqn. (2) and is obviously related to the height and to the gravitational force. If the difference in potential is zero we say that the top of the liquid in each vessel is at the same level.

In exactly the same way, we can define a chemical potential, μ, for a given element, say, carbon or oxygen, such that the difference in its value in two states is the tendency for that element to move. The difference, $\Delta\mu$, is given by eqn. (2), dn now referring to the transfer of a given number of atoms, or pairs of atoms, from state (1) to state (2). Experimental determination of the work involved in this transfer is more difficult than with electrons, but the theoretical determination is satisfactorily rigid. From what has been said already, it follows that the chemical potential has a heat term and a restriction term. The first is generally known as the heat content term H, and the second as the entropy term $-ST$. The minus sign in the entropy term comes in because S is a measure of freedom or disorder, the opposite of restriction.

The simplest and most important part of the entropy term concerns restriction of volume. If we wish to know the difference in oxygen potential between a gas mixture where the partial pressure of oxygen is P_1 and another at the same temperature but at a pressure P_2, then by derivation from the simple gas laws

$$\Delta\mu = -\frac{dw}{dn} = RT \log_e P_2/P_1 \quad . \quad . \quad . \quad (3)$$

Between these two states, there is no difference in heat content but there is in the degree of restriction. The gas mixture with the higher oxygen partial pressure (greater restriction) is at a higher oxygen potential than the other.

The other type of restriction concerns rotation, vibration, etc.; escape from restriction here manifests itself in an increase of the specific heat which forms an important part of entropy.

If the oxygen in a gas mixture is in equilibrium with a liquid or solid phase, then the oxygen potential in this condensed phase is equal to that in the gas phase and can be given the value $RT \log_e P_{O_2}$, assuming arbitrarily a zero of potential at P = unity. If the oxygen potential of the condensed phase is lowered, then oxygen will move into this phase; if increased, it will move out. The *extent* to which this happens is dependent on the effect of this movement on the chemical potential of each phase and on the bulk of the phases present. This capacity effect is discussed later. The *rate* at which this happens cannot be predicted from the thermodynamic approach but only from the kinetic.

The equilibrium oxygen pressure over an oxide of a metal in contact with the metal is a constant at any one temperature and, therefore, the oxygen potential of this oxide — metal system is fixed. Where the oxide is in equilibrium with the metal, then the latter must contain some oxygen in solution, the potential of which must be the same as that of the gas, i e., $= RT \log_e P_{O_2}$.

Experimentally, it is found that for any concentration of oxygen in a metal, below that at this three-phase point, the equilibrium vapour pressure falls as the square of the concentration. The oxygen potential of this solution, therefore, is given by

$$\mu_{O_x} = 2\, RT \log_e [O] + \text{constant} \quad . \quad . \quad . \quad (4)$$

where [O] is the concentration of oxygen in the metal.

As we have seen above, many oxides of metals are known to exist over a small range of composition lying across that corresponding to their formula. This is now considered to be a much more general phenomenon than has previously been believed. The lower limit corresponds to equilibrium with the metal and oxygen, the upper being much less definite as it depends on a complex function of the pressure of oxygen. At all events, because of this phenomenon, one can transfer small quantities of oxygen to or from a metal oxide without introducing the metal phase and, accordingly, we have a range of two-phase equilibria, oxide — oxygen gas, permitting us to *assign to the oxide* at the composition of the formula *a definite oxygen potential.* In general, when this term is used, it refers to the composition as given by the formula but it should be remembered that conditions are frequently found where the potential of oxygen in the oxide departs significantly from this value.

Some Applications of Chemical Potentials. One of the commonest ways of lowering the oxygen potential of a gas is to lower the oxygen content by equilibrium with carbon or with carbon monoxide. The values so obtained are generally low but of the right order of magnitude for metallurgical processes. At a total pressure of CO and CO_2 of one atmosphere and in the presence of solid carbon, the oxygen potential is fixed for any one temperature according to the reactions, $C + O_2 \rightleftharpoons CO_2$, or $2C + O_2 \rightleftharpoons 2CO$, which ever gives the lower potential. In the absence of solid carbon, the oxygen potential can be controlled over a very wide range by varying the CO_2/CO ratio.

Thus at, say, 1200° c., FeO can be reduced to Fe with pure CO, but in the presence of 30 % CO_2, no reaction can take place because the potential of the oxygen in the two phases is the same. If the CO_2/CO ratio is raised to unity, the surface of iron will be oxidised to FeO but a small leak of air into the system would raise the oxygen potential of the gas such that Fe_3O_4 or Fe_2O_3 would be formed. In the process of "blueing" steel, the oxygen potential of the gas must be controlled so that a compact layer of FeO only is formed. (This changes partly to Fe_3O_4 on cooling.)

At the same time, this gas mixture has a carbon potential which specifies the carburising or decarburising power of the gas. It is not possible to link this to a vapour pressure of carbon because this is immeasurably low but a suitable zero of potential can be taken as that of pure graphite. Oxygen and nitrogen can be removed from combination with some metals simply by evacuating or by reducing and maintaining the pressure below that of the chemical potential in the metal. This cannot be done for carbon because of its low equilibrium pressure but the potential of carbon can be lowered by the addition of oxygen because the carbon and oxygen potentials are interlocked inside the gas phase by the chemical equilibria between them; the higher the oxygen potential, the lower the carbon and vice versa. Inside the metal or other condensed phase, the interlocking is rather more complicated and the major part of the thermodynamic studies of metallurgical processes is aimed at a knowledge of this and other types of interlocking.

Chemical Potentials in Metastable Systems. However, there are some very important cases where there is no equilibrium or interlocking in the gas phase but rather a metastable equilibrium with a solid. At 500° c., the nitrogen content of iron corresponding to equilibrium with one atmosphere of nitrogen is of the order of 1 to 10 atoms per 10,000 of Fe. It is not surprising that it is impossible to obtain a nitrogen potential in N_2 gas sufficient to raise the N content of iron by very much, particularly as this content only rises as the square root of the N_2 pressure. However, iron nitrides containing more than 30 N atoms per 100 Fe can readily be prepared at this temperature by the action of NH_3, providing the H_2 is kept low. Measurements of the nitrogen potentials of these nitrides are not very accurate but values of the order of $RT \log_e 10^5$ are indicated. Despite this high value of the N potential, nitrogen passes from the gaseous state to the solid and therefore must be at a higher potential in the former state. The potential of nitrogen in the gas should strictly speaking be measured only under conditions of equilibrium and from the actual partial pressure of N_2 given by the relation $P_{N_2} = K_T P^2_{NH_3}/P^3_{H_2}$. However, at 500° c., the reaction, $2NH_3 \rightleftharpoons N_2 + 3H_2$, is negligibly slow in comparison with the reaction, $2NH_3 \rightleftharpoons 2N(\text{in Fe}) + 3H_2$, which proceeds readily, in the forward direction if P_{NH_3} is high and P_{H_2} low and in the reverse direction if the pressures are reversed. The nitrogen potential clearly is related to these two pressures, just as the oxygen potential is related to P_{CO} and P_{CO_2}, whether or not the equilibrium pressures of N_2 or O_2 exist. There exists, therefore, a chemical potential for nitrogen in ammonia-hydrogen mixtures given by $RT \log_e K_T . P^2_{NH_3}/P^3_{H_2}$ which for P_{H_2}, equal to, say, 10^{-3} atoms, is equal to $RT \log_e 10^9$ at 500° c. This value is amply in excess of that of nitrogen in iron nitride and accordingly ammonia can nitride iron by a "downhill" process. It can and does eventually go much further downhill to the state of $N_2 + 3H_2$ but it "prefers" to go by the intermediate stage of iron nitride.

The Iron-Making Process. It is of interest to follow the oxygen potentials involved in making iron in the blast furnace. The essential data are given in Fig. 2, which is a less detailed form of a diagram given later in the Discussion.[11] The solid lines give the O potentials as determined from the P_{O_2} in equilibrium with the two phases indicated (where one of these is CO or CO_2 gas, the pressure of each is one atmosphere). The problem in iron-making is to submit the oxides of iron to contact with a gas whose temperature is high enough to provide plenty of molecules with the energy of activation, and whose oxygen potential is below that of the respective oxides. If one could provide a separate source of heat, it would, of course, be sensible to start with a gas containing a high percentage of CO and thus a very low pressure of O_2, and this is done in the sponge iron process. In general, however, it is simpler to provide the heat and the gas from the same reaction, the burning of carbon, and accordingly, in the blast furnace, air, whose conditions correspond to the point *a* on the diagram, is injected at the bottom of the furnace.

If we follow a "packet" of this air through the furnace, we will travel along the broken line, first with a rapid rise in temperature due to combustion, then with a rapid fall in oxygen potential until we are near to the equilibrium point with carbon. The "packet" soon meets a lump of iron ore (now down to FeO in this part of the furnace) which gives up oxygen to the gas. As the "packet" travels up the furnace, its temperature drops and its oxygen potential is pulled down by the carbon and up by the ore (now in the form of the higher oxides Fe_3O_4 and Fe_2O_3). The gas has been cooling all the while as it meets the descending burden. Finally at about 800° C. the reaction has become too slow and the equilibrium between CO and CO_2 which determines the O potential is frozen at a point near that shown at *b*. From there until the point *c* where the gas leaves the top of the furnace, there is only a change in temperature.

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[11] Dannatt and Ellingham, This Discussion.

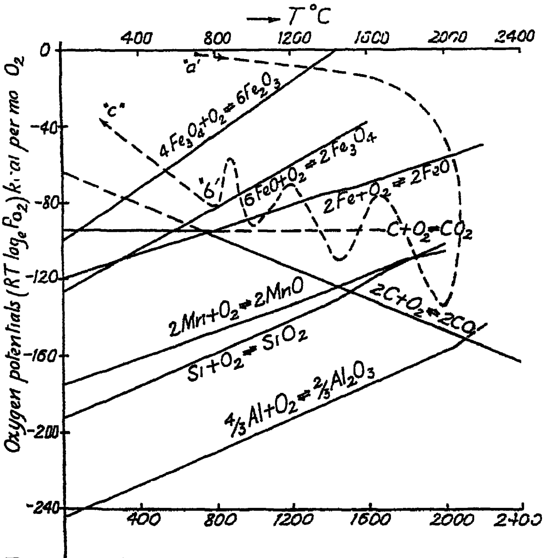

FIG. 2.—The broken line shows the history of a "packet" of air from its entry into the blast furnace at "*a*" to its discharge at "*c*." The curves for oxides of Mn, Si and Al are included to show the deoxidising power of these elements.

This picture illustrates only one aspect of the several which are of importance to the theory of the blast furnace but it does predict one important point. It is of great economic importance to achieve the highest possible O potential (low CO) of the exit gases, that is, *b* should be as high as possible. This will happen if the carbon gives up its struggle to lower the O potential before the ore gives up its struggle to raise it. This the carbon will do if the temperature at which it ceases to react with CO_2 is higher than that at which the iron oxides cease to react with CO.

Potential and Capacity

While the chemical potential is sufficient in itself to determine which way a reaction will proceed (if at all), being an intensity factor it can tell us nothing as to the extent of the possible reaction. For this we need a capacity factor. If we put electrons into a condenser, the electrical potential rises. At any voltage, the number of electrons required to raise the potential by unity is a constant known as the capacity of the condenser. Similarly, if we put oxygen into liquid iron, the oxygen potential rises but in this case logarithmically as in eqn. (4) rather than linearly as in the case of the condenser.

We may consider our condenser or our sample of liquid iron as "vessels" with shapes as shown in Fig. 3 (*a*) and (*b*) respectively. As we pour electricity or oxygen into the vessels, the potential rises but more oxygen is required at the higher potentials to produce a given rise; the capacity increases as we go up. If the vessel is filled to any particular level, the amount of electricity or oxygen is simply the area under this level.

(Another parallel case but in different dimensions is that of temperature and specific heat as shown in Fig. 4. These two quantities are potential and capacity factors respectively and the area up to any temperature level is the total heat content.)

The capacity of iron for oxygen can be expressed quantitatively in a parallel way to that of a condenser, using the relation of eqn. (4):

$$\text{Capacity} = \frac{dn}{d\mu} = \frac{V d[O]}{d\mu} = \frac{V[O]}{2RT} \quad . \quad . \quad . \quad (5)$$

where n is the amount of oxygen present and V the volume of the liquid iron. The scale on the right in Fig. 3 (b) is the same as that in Fig. 2, but the scale used for plotting has, of necessity, been expanded about twelve times.

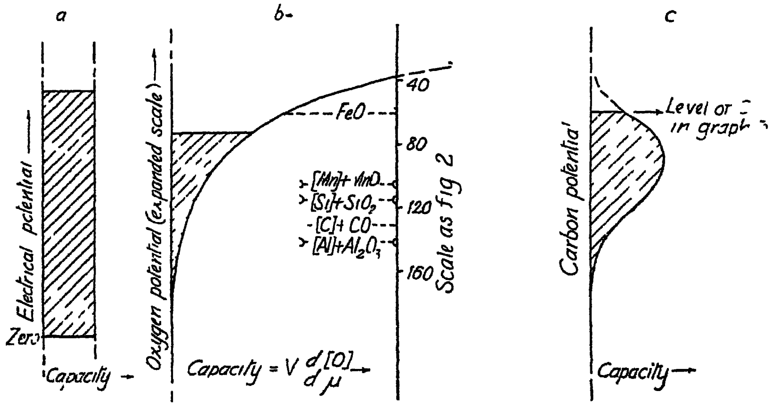

FIG. 3.—The capacity of various systems as a function of the potential (a) Electrons in a condenser; (b) Oxygen in Iron; (c) Carbon in Iron. The area under any level is the amount of material present.

While the "walls" of our vessels have no definite upper limit, there are very real chemical limits. The potential of oxygen in FeO at 1600° c., as given in Fig. 2, lies at −70 kcal. Any attempt to put oxygen into iron above this limit will just result in the formation of FeO. In other words, there is a "leak" at this level into another phase with an unlimited capacity; the whole of the iron could be burned away at this oxygen potential.

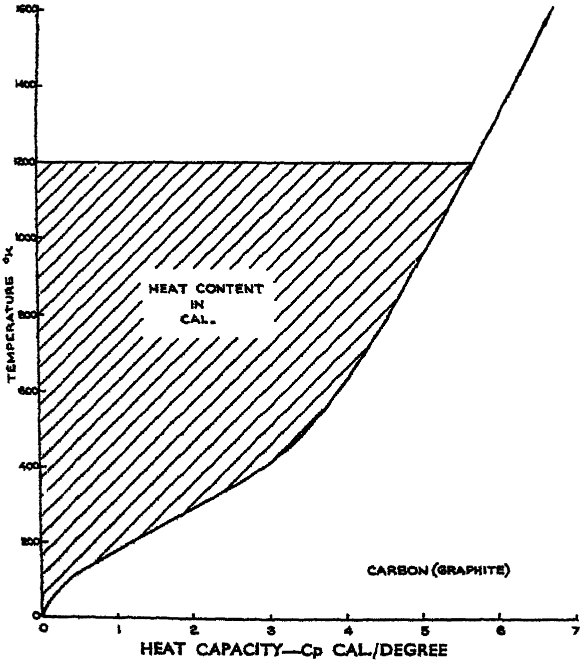

FIG. 4.—The capacity of carbon to take in heat as a function of the temperature (potential)

Similarly, if the iron was saturated with carbon, it would not be possible to raise the oxygen potential above −130 kcal. without producing supersaturation with respect to CO. The leak here is into the gas phase. As the carbon potential falls, however, the permissible oxygen potential goes up. In this case, the interlocking is simple in that $\mu_{O_2} + \mu_{2C}$ = constant. The carbon can be "blown out" with oxygen in a Bessemer converter until the oxygen potential rises to −70 kcal. where it will burn the iron to FeO. At this point, the potential of 2C will be −60 kcal. with respect to that of a saturated solution at 1600° c. The carbon concentration corresponding to this potential has been found to be 0·01 wt.-%.

This burning of iron would put a limit on the possibility of removing carbon from iron, were it not for the fact that one can lower the level of the leak by lowering the pressure. (The above values are for 1 atm. CO.) Iron with a low content of carbon and oxygen can be prepared under high vacuum. The presence of an inert gas can assist in obtaining the necessary very low partial pressure of CO.

Activities and Activity Coefficients

In the case of carbon, we have obtained a convenient zero for the chemical potential because of the fact that saturation occurs with the pure solid. Many other elements, as we have seen, are miscible in all proportions and therefore a definite link between the chemical potential of that element in solution, and the zero, chosen as that of the pure substance, is not possible. Furthermore, it is found that the potentials of most elements in solution, except for very dilute solutions, do not follow the simple logarithm-of-concentration law as illustrated by eqn. (4) for oxygen.

Basically, this is due to the fact that the vapour pressure of that element does not bear a linear relation to the concentration, throughout the range from dilute solution to the pure element; i.e., Raoult's law is not obeyed. In order to make use of the fundamental equation (3), it becomes necessary to define a parameter dimensionally the same as concentration but which *does* bear a linear relation with the vapour pressure and can thus be used in the specification of the chemical potential. This quantity is the activity a and is related to the concentration by the activity coefficient f by the relation:

$$a = fc \qquad . \quad . \quad . \quad . \quad . \quad (6)$$

Much of the physical chemistry covered by this Discussion is concerned with the factors which determine the activity coefficient.[12] In general, forces of attraction between the solute atoms or molecules themselves or between them and the solvent lead to increased values of f, and forces of repulsion to decreased values.

The chemical potential now becomes

$$\mu = RT \log a + \text{const.} = RT \log fc + \text{const.} \qquad . \quad . \quad (7)$$

and the capacity

$$\frac{Vdc}{d\mu} = \frac{Vc}{RT} - \frac{Vc}{f}\frac{df}{d\mu} \qquad . \quad . \quad . \quad . \quad (8)$$

From the measured and extrapolated values for the activity of carbon dissolved in iron, the curve in Fig. 3 (*c*) has been drawn. The contrast between this curve and that in Fig. 3 (*b*) is striking. The lower part of the curve is the same, which means that, for small additions to pure iron, carbon behaves normally. Before long, however, the normal increase in capacity is not kept up and indeed a decrease occurs at higher concentrations; all of the spaces in the iron available to take up carbon are becoming filled. As before, the potential of the carbon in the iron cannot rise above that of pure graphite.

Conversely to this example, the addition of a substance, which has an affinity for the element (or compound) whose chemical potential is being studied, lowers the value of f and produces a "bulge" outwards in the capacity curve. If there is a fixed amount of the element present, the top level, if it is above the bulge, will fall as the element fills this bulge.

As it is not possible as yet to fix definitely the *position* of what might be considered as the "normal" capacity curve, it is not always possible to say whether a curve has a bulge in one place or a constriction in another. This provides plenty of scope for argument about the formation, or otherwise, of chemical compounds. For example, are the spaces available for carbon in iron really opportunities to form Fe_3C or does the carbon atom combine with the mass of the iron and exert a repulsive force towards any carbon neighbours? Certainly, the tendency in solid iron for interstitial atoms to form superlattices with the maximum separation and for one interstitial element to lower the capacity available to the other is somewhat easier to visualise on the basis of repulsive forces. However, an increase in a repulsive force is not yet really distinguishable from a decrease in an attractive force and therefore the choice is not very important.

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[12] See, for example, Chipman ("Activities in Liquid Metallic Solutions"), This Discussion.

Slag Refining. So far our attention has been concentrated on the movement of elements or compounds between the metal and the gas phases. Much of process metallurgy is concerned with movement between a metal and a slag phase as in the third section of this Discussion. We have oxygen, sulphur, phosphorus, etc , potentials of the slag and a capacity curve for each but of a more complex shape. Of course, these elements will always tend to move to the slag if their potential there is lower than it is in the metal. We can picture the process of refining, say, for sulphur, as the connecting of two "vessels" by a bridge for sulphur followed by a flow until the top level of our "fluid" is the same in both vessels. The *rate* at which this flow takes place has already been discussed in Part II of this paper.

The shape of the curves in Fig. 3 (*b*) and (*c*) gives a simple picture of the fact that it is easy to remove a large amount of an element when its potential is high but very difficult when it is low. We can also see from these that an increase of the volume of the slag or the addition of some substance which will bulge out the curve at a low level of potential will both help to draw an element into the slag. From these curves, one can work out the optimum conditions for double slagging ; the second slag requires a greater capacity at a low potential than does the first.

Deoxidation of Steel. As we have seen, liquid steel from which most of the carbon has been removed by oxidation contains oxygen up to a potential near that of FeO. On cooling, this oxygen combines with the remaining carbon and bubbles off as CO, the steel formed being called "rimming steel." However, most steels are partly or wholly deoxidised or "killed" by the addition of such elements as manganese or aluminium which open a "leak" in the potential-capacity curve as shown in Fig. 3 (*b*). These combine with all of the oxygen above the level of the leak and form an oxide which separates as a distinct slag phase; in the case of aluminium, the deoxidation is effectively complete, the remaining oxygen being about 10^{-5} %. As the elements themselves are soluble in iron and the oxides produced are soluble in the slags, their activities are variable and are related to the concentrations used. The level of a leak is thus not fixed as in the case of FeO but covers a band for each element as shown by the brackets in the figure. The bands are placed to cover the ranges of concentration in which these elements are usually found.

Chemical Potentials in Single-Phase Equilibria

The reader used to the conventional method of introducing chemical thermodynamics will be surprised that homogeneous equilibria so far have barely been referred to. In process metallurgy these are, however, of secondary importance to the movement or partition between two phases. Nevertheless, equilibria in single-phase systems are of great importance because they control the external relations of that phase. Unfortunately, practically no methods exist for determining the actual molecular species and their amounts present in metals and slags. The most reliable studies of these equilibria are based on studies of the chemical potentials of the species by equalising these to a gaseous phase where they can be measured, and then by measuring the interlocking of the potentials. The interlocking is expected to follow the well-known law of mass action and much work has been done to show when this happens or what activity coefficients must be introduced to make it happen. However, the form of the interlocking is the thing that really matters in process metallurgy and the exact chemical nature of each species in the equilibria is of secondary importance.

Chemical Potential, Activity, Free Energy

The reader of thermodynamics may easily become confused with the many terms used. Activity and chemical potential are closely related, the latter varying simply as $RT\log_e$ of the former. The potential has the advantage of being of wider use than the activity as it is easier to fix a point of reference of potential between two phases than it is to link activities. It is also easier to calculate the chemical potential (on the basis of its components, the heat term and the entropy term) than it is activity. Indeed, chemical potentials can sometimes [13] be determined directly from an electrical potential of a cell

In most papers on thermodynamics in chemistry, the term free energy is used. Usually, this refers to the Gibbs free energy and is associated with a particular chemical equation. It is not proposed here fully to compare this term with chemical potential except to say that, in reactions involving the transfer of a given species from one phase to another, *the two terms are identical* In all other usage, they are closely related

There are many advantages in the use of the concept of chemical potential as against free energy. The term potential unambiguously suggests an intensive factor whereas the term energy is, except in this case, invariably used as an extensive factor. (Some authors also use the term free energy as an extensive factor.) Furthermore, by its association with electrical and gravitational potentials, it is automatically visualised as a driving force for something to happen. Its use focuses attention on the movement of the particular species of primary importance in the metallurgical process, whereas the use of free energy brings too much into prominence chemical equations which are often so numerous that they obscure the picture. Finally, it permits the introduction of a " capacity " to describe the ability of a given phase to take up the species at each particular potential level.

Conclusion

In laying out here the principles of physical chemistry, the author has had to select ways which he believes to be simplest to understand and yet which are sufficient to form a firm foundation for the subject. Some of the alternative ways of dealing with these principles will be referred to in other papers of this Discussion. The subject has been allowed by some authors to grow to great complexity with a consequent loss to the many whose work would benefit by its application. It is hoped that this Discussion will bring out the fact that the essential principles are really quite simple.

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[13] Rose, Davis and Ellingham, This Discussion.

I. METALLIC SOLUTIONS

ACTIVITIES IN LIQUID METALLIC SOLUTIONS

BY JOHN CHIPMAN

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Equilibrium

In a substantial fraction of the high temperature processes of metallurgy the limitations within which the process must operate are prescribed by conditions of equilibrium. No process can be carried beyond a state of equilibrium and it is only by adjustment of the factors which control the equilibrium that the completeness of these metallurgical processes may be controlled. Processes must operate at finite rates if they are to be profitable and hence equilibrium in the rate-controlling steps must be avoided. Even in such cases, however, a knowledge of the actual condition of equilibrium in each step of the process is essential to the application of reaction rate theory. Such considerations as these have led process metallurgists to take a lively interest in studies of equilibrium, at least with respect to such systems as are of current or potential practical importance in the production of metals.

The condition of equilibrium in a system which is maintained at a fixed temperature and pressure is described thermodynamically by the requirement that the free energy of the system be a minimum. Applied to a chemical reaction this means that when the reaction occurs under equilibrium conditions the change in free energy is zero. As an example, in the reaction

$$\mathrm{C\ (graphite)} + \mathrm{CO_2}\ (g) = 2\ \mathrm{CO}\ (g) \quad . \quad . \quad . \quad (1)$$

the equilibrium condition at constant temperature and pressure is defined by the equation

$$\Delta G = 0 = 2\,G_{\mathrm{CO}} - G_{\mathrm{C}} - G_{\mathrm{CO_2}} \quad . \quad . \quad . \quad (2)$$

in which the G's represent the molal free energies of the respective substances. Now these molal free energies or chemical potentials are, in the case of gaseous substances, related to the partial pressures by equations of the form

$$G_{\mathrm{CO}} = G^{\circ}_{\mathrm{CO}} + RT \ln p_{\mathrm{CO}} \quad . \quad . \quad . \quad . \quad (3)$$

where G°_{CO} is the standard free energy at unit pressure (normally at 1 atmosphere pressure), R is the gas constant and $\ln p_{\mathrm{CO}}$ is the natural logarithm of the partial pressure. Since the free energy of a solid is only very slightly affected by changes in pressure, the value of G_{C} may be considered independent of the partial pressures of the two gases. One may substitute values of G for the gases as given in (3) into (2) to obtain

$$\Delta G = 0 = 2\,(G^{\circ}_{\mathrm{CO}} + RT \ln p_{\mathrm{CO}}) - G^{\circ}_{\mathrm{C}} - (G^{\circ}_{\mathrm{CO_2}} + RT \ln p_{\mathrm{CO_2}})$$

Now if we define ΔG° in the same manner as ΔG was defined in (2), the above expression simplifies to

$$\Delta G^{\circ} = -RT \ln \frac{p^2_{\mathrm{CO}}}{p_{\mathrm{CO_2}}} = -RT \ln K \quad . \quad . \quad . \quad (4)$$

Here ΔG° is the increase in free energy in the reaction when each substance used or produced is in its standard state. At any given temperature it has a fixed value.

This is the derivation of the law of mass action and the ratio $p^2_{\mathrm{CO}}/p_{\mathrm{CO_2}}$ typifies the equilibrium constant of the mass law. In deriving it we have neglected the effect of pressure upon the solid carbon and have assumed in (3) that the gases are ideal. At quite high pressures these assumptions are not valid and the ratio which we have called the equilibrium constant ceases to be a constant.

In the early application of the mass law to reactions which occur in solutions, the pressure terms were replaced by molal concentrations. In many instances this procedure yielded constants which appeared to be actually constant over a range of concentrations. In many other cases however, the " constant " proved to be highly variable and its deviation was far greater than could be explained by experimental errors. Now I know of no circumstance which is quite so embarrassing to a physical chemist as the existence of a " constant " of unexplainable variability. The situation was saved at the turn of the century by G. N. Lewis[1] in the invention of the functions, fugacity and activity. The first of these is nothing more than a corrected pressure which becomes equal to the pressure when the gas becomes ideal. Since at high temperatures and moderate pressures the gases which take part in metallurgical reactions do not depart significantly from the ideal behaviour, we shall here neglect the distinction between fugacity and pressure and proceed to a consideration of the activities of substances in solutions.

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[1] Lewis, *Proc. Amer. Acad.*, 1901, **37**, 49; 1907, **43**, 259.

Activity.—Consider two solutions of the same components at the same temperature but of different concentrations and let one of these be accepted as a standard reference state. Let p_i and p_i° be the partial pressures of component i in the vapour in equilibrium with the two solutions, the second being the standard. The activity of component i in the first is then defined by the equation *

$$a_i = p_i/p_i^\circ \quad . \quad . \quad . \quad . \quad . \quad (5)$$

It is evident that the activity of i in the standard solution is unity. The relationship between the activity and the chemical potential μ_i (which is the same as the partial molal free energy $\overline{G}_i$, and is equal to the molal free energy G_i of the vapour in equilibrium with the solution) is obtained by applying equations of the type of (3) to the vapour at the partial pressures of eqn. (5). This yields

$$\mu_i - \mu_i^\circ = RT \ln \frac{p_i}{p_i^\circ} = RT \ln a_i \quad . \quad . \quad . \quad (6)$$

where μ_i° is the chemical potential of i in the solution which was chosen as standard, i.e., the solution in which $a_i = 1$.

An *ideal solution* is defined as one in which there is no heat of mixing, and no volume change and in which the partial pressure of each component obeys Raoult's law:

$$p_i = N_i p_i^\circ \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where N_i is the mole fraction in the solution and p_i° the vapour pressure of the pure component i. This makes pure i the standard reference state and requires that, in an ideal solution, $a_i = N_i$. It follows that in an ideal solution

$$\mu_i - \mu_i^\circ = RT \ln N_i \quad . \quad . \quad . \quad . \quad (8)$$

Another important characteristic of an ideal solution is expressed in the partial molal entropies of its components. From the basic thermodynamic relationship [2]

$$\mu_i = \overline{H}_i - T\overline{S}_i \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and from the fact that $\overline{H}_i - \overline{H}_i^\circ = 0$, since there is no heat of mixing, it follows that

$$\overline{S}_i = S_i^\circ - R \ln N_i \quad . \quad . \quad . \quad . \quad (10)$$

This is exactly the value required by statistical mechanics for a solution in which the mixing of the several kinds of molecules is completely random.

Non-ideal Solutions.—Metallic solutions generally deviate from Raoult's law. Attractive forces between unlike atoms, as frequently exhibited by formation of intermetallic compounds, give rise to negative deviations. Where these attractive forces are smaller than those between like atoms, positive deviations occur. In either case, a_i is not equal to N_i. The ratio a_i/N_i is given the symbol γ_i and is called the activity coefficient. The deviation of γ_i from unity is a simple measure of the departure of the solution from ideal behaviour.

Both activity and activity coefficient change with the temperature in accordance with the equation

$$\frac{d \ln a_i}{dT} = \frac{d \ln \gamma_i}{dT} = \frac{-\overline{L}_i}{RT^2} \quad . \quad . \quad . \quad . \quad (11)$$

where $\overline{L}_i = \overline{H}_i - \overline{H}_i^\circ$ is the partial molal heat content of i referred to the chosen standard state. In any solution in which the heat of mixing is zero the activity is independent of temperature.

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[2] Lewis and Randall, *Thermodynamics* (McGraw-Hill, New York, 1923).

* More rigorously the p's are the corrected pressures or fugacities.

The concept of the *regular solution* was introduced by Hildebrand[3] in 1927. In such a solution the distribution of molecules is completely random and hence statistical mechanics requires that the entropy of each component be that given by eqn. (10). The heat of mixing may be positive or negative and this determines the deviation from Raoult's law. By means of (6), (9) and (10) it may be shown that for such a solution

$$RT \ln \gamma_i = \bar{H}_i - H^\circ_i = L_i \quad . \quad . \quad . \quad . \quad (12)$$

Another important property of a binary regular solution is expressed in the following equation which connects the chemical potential of one component with the mole fraction of the second

$$\mu_1 \text{ (regular)} - \mu_1 \text{ (ideal)} = b\, N_2^2 \quad . \quad . \quad . \quad (13)$$

where the constant b is independent of the concentration. Hildebrand and Wood[4] have shown that an equation of this form is derivable from statistical mechanics for a regular solution provided (1) the molecular volumes are equal, (2) the attractive potential is inversely proportional to the sixth power of the intermolecular distance, (3) the energy of mixing is only that due to this potential and (4) that the potential between unlike molecules is the geometric mean of that between like molecules. Many pairs of organic liquids are known whose solutions follow quite closely the regular behaviour prescribed by (13).

Semi-regular Solutions.—In metallic systems it is not to be expected that solutions will always conform to regular behaviour. In fact regularity implies lack of order and absence of any tendency toward compound formation which immediately rules out many interesting metallic systems. Many metallic solutions do conform surprisingly well with both (10) and (13) though not at all concentrations. We shall call these semi-regular solutions. If departure from regularity is due to ordering it is evident that some sort of disorder parameter must be introduced into eqn. (10). The entropy of a component of such a solution has the value

$$\bar{S}_i = \bar{S}^\circ_i - DR \ln N_i \quad . \quad . \quad . \quad . \quad (14)$$

and the parameter D has a value of unity in a completely disordered, hence regular, solution.

On theoretical grounds (13) can be extended to components of dissimilar molecular volume by substituting volume fraction for mole fraction. In the few cases involving metallic solutions of unlike atomic volumes in which the experimental data are sufficient, it is found that this substitution does not diminish the departure from regularity. The effect of volume appears to be small compared to deviation from the assumptions made with respect to interatomic potential. Eqn. (13) does not always fit the facts even approximately over a wide range of concentration. It does, however, express the behaviour of *dilute* metallic solutions remarkably well and we shall define a semi-regular solution as one which conforms to this equation at each end of the composition range. A more useful form of the equation is obtained by combining it with (6) and (8) to obtain

$$RT \ln \gamma_1 = b\, N_2^2 \quad . \quad . \quad . \quad . \quad (15)$$

Activity from Vapour Pressure

The most direct method for establishing activity is the measurement of vapour pressure. This method has been applied extensively to studies of the *amalgams*, for which it is especially well adapted on account of the high vapour pressure of mercury. The earliest complete study of a system by vapour-pressure measurements was that of Hildebrand[5] on zinc amalgams.

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[3] Hildebrand, *Proc. Nat. Acad. Sci.*, 1927, **13**, 267.

[4] Hildebrand and Wood, *J. Chem. Physics*, 1933, **1**, 817.

[5] Hildebrand, *Trans. Amer. Electrochem. Soc.*, 1912, **22**, 319.

Hildebrand and Eastman [6] measured vapour pressures of mercury over its alloys with gold, silver and thallium at temperatures near the boiling point. The activity of mercury in thallium amalgams, at 325° C., as computed by (5), is shown in Fig. 1. It is evident that the departure from ideality is not great. The logarithm of the activity coefficient, a/N, is plotted against the square of the mole fraction of thallium in Fig. 2. The curve is fairly typical of semi-regular solution behaviour, approaching a linear relationship at either end and curving smoothly in the intermediate range. The quantity b in eqn. (15) varies considerably over the composition range and the solution is therefore not regular. Limiting values of b at the extremities are, at the mercury end, approximately 2000 and at the thallium end 265. In dilute solutions the value of b is exceedingly sensitive to small errors of measurement and few data exist which are good enough for accurate extrapolation to zero concentration. Conversely, calculated activity coefficients at low concentration are insensitive to errors in b and roughly approximate values of this quantity are therefore sufficient.

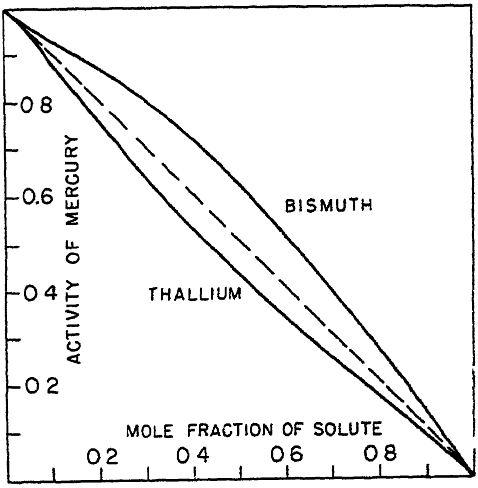

FIG. 1.—Activities of thallium and bismuth in amalgams at 325° C., showing typical deviation from Raoult's law.

A summary of activity coefficients [5] [6] [7] [8] [9] [10] [11] of mercury in liquid amalgams at temperatures near the boiling point of mercury is given in Fig. 3. The type of plot used here is a very convenient means of recording deviations from ideal behaviour. It shows also deviations from regularity, indicating that in general the amalgams behave as semi-regular solutions.

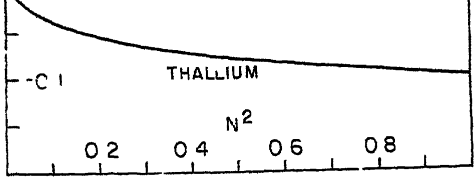

FIG. 2.—Logarithm of the activity coefficient of mercury as a function of the square of the mole fraction of bismuth and thallium, illustrating semi-regular solutions.

Molten Brass.—The activity of the volatile component when the second is non-volatile may also be determined from the boiling point of the solution. Measurements of the boiling points of copper-zinc alloys reported by Hansen,[12] Lohr and Popoff[13] were employed by Johnston[14] to estimate the activity of zinc in molten brasses. These data, along with more recent vapour-pressure measurements of Schneider and Schmidt[15] may now be re-examined in the light of the regular-solution equation. The activity of zinc at the boiling point of brass is equal to the reciprocal of the vapour pressure of pure zinc in atmospheres at the same temperature, the values being obtained from Kelley's tables.[16] Two recent studies of the vapour pressure of zinc in solid brasses by Hargreaves[17] and by Seith and Kraus[18] may be extrapolated to yield data on molten brass. Hargreaves' data at 902° extrapolated to 32 atom % zinc indicate a pressure of 95 mm. which is equal to that of a liquid brass containing 37 atom %.[19] Similarly the data of Seith and Kraus at 850° are extrapolated to yield a pressure of 133 mm. over β-brass of 53 or a liquid of 56 atom % zinc. These two extrapolations, together with the vapour pressure of pure zinc, lead to activity coefficients of 0·37 and 0·57 respectively.

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[6] Eastman and Hildebrand, *J. Amer. Chem. Soc.*, 1914, **36**, 2020 ; 1915, **37**, 2452.
[7] Bent and Hildebrand, *J. Amer. Chem. Soc.*, 1927, **49**, 3011.
[8] Hauffe, *Z. Elektrochem.*, 1940, **46**, 352.
[9] Millar, *J. Amer. Chem. Soc.*, 1927, **49**, 3003.
[10] Pedder and Barratt, *J. Chem. Soc.*, 1933, 537.
[11] Hildebrand, Foster, and Beebe, *J. Amer. Chem. Soc.*, 1920, **42**, 545.

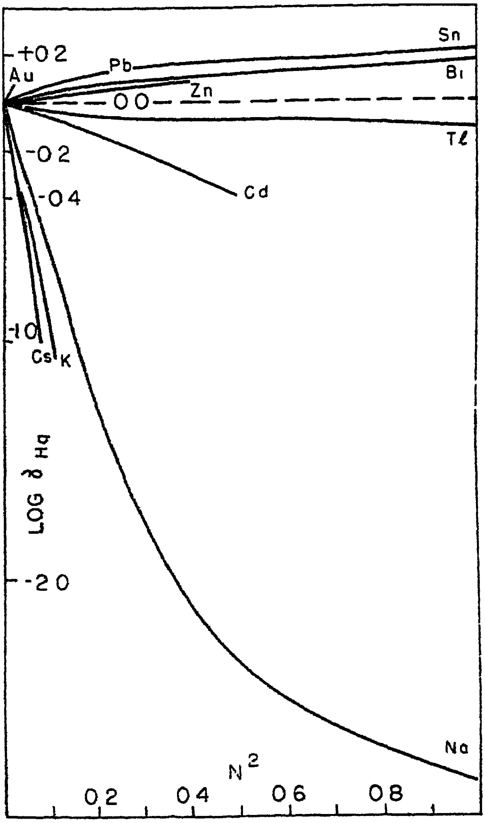

FIG. 3.—Activity coefficients of mercury in various amalgams near the boiling point of pure mercury.

Since the data cover a range of 850° to 1365° it is scarcely safe to neglect, as Johnston did, the effect of temperature on the activity coefficient. A better approximation is obtained by assuming, as Scatchard and Hamer[20] have done in a similar case, that b of eqn. (15), and hence $RT \ln \gamma_{Zn}$, are independent of temperature. A plot of $RT \ln \gamma_{Zn}$ against N^2_{Cu} is shown in Fig. 4, the straight line being sufficient to represent all of the data within the rather wide limits of experimental uncertainty. From this line, values of the activity and activity coefficient of zinc in molten brass at 1200° c. have been computed and are shown in Fig. 5.

The boiling points of brasses containing from 10 to 60 % zinc, computed from the straight line of Fig. 4, are shown in Table I. These values obviously cannot be more accurate than the average data from which they were computed, or about ±25°. However, they represent average values based upon several sets of data and are therefore probably more dependable than any one set. Further experimental work would be needed to improve the accuracy of these data and to establish the dependence of the quantity *b* on temperature and composition

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[12] Hansen, *Trans. Amer. Inst. Met*, 1912, **6**, 110.
[13] Lohr and Popoff, quoted by Gillett, *U.S. Bur. Mines Bull.* No. 73, 1914, p. 126.
[14] Johnston, *Trans. Amer. Inst. Min. Met. Eng.*, 1919, **60**, 417; *Int. Crit. Tables*, **3**, 284.
[15] Schneider and Schmidt, *Z. Elektrochem.*, 1942, **48**, 627.
[16] Kelley, *U.S. Bur. Mines Bull.* No. 383, 1935.
[17] Hargreaves, *J. Inst. Metals*, 1939, **64**, 115.
[18] Seith and Kraus, *Z. Elektrochem.*, 1938, **44**, 98.
[19] Raynor, *Annotated Equilibrium Diagrams No.* 3 (Inst. of Metals, 1944).
[20] Scatchard and Hamer, *J. Amer. Chem. Soc.*, 1935, **57**, 1809.

TABLE I

Calculated Boiling Points of Copper-Zinc Alloys

% Zinc	10	15	20	30	40	50	60
Boiling Point ° c. ..	1410	1320	1260	1165	1095	1040	995

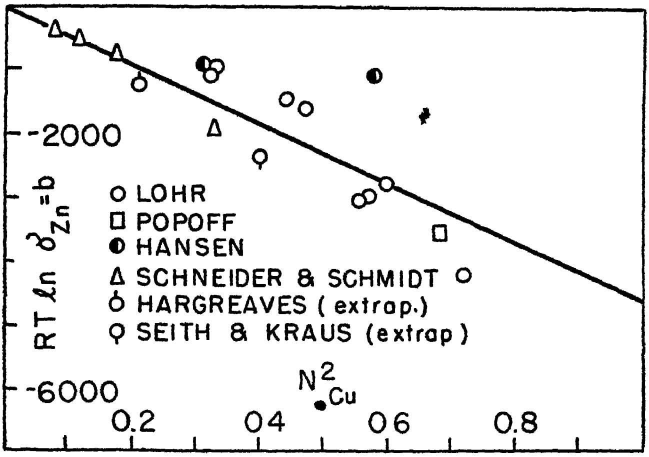

Fig. 4.—Values of *b* or *RT* ln γ_{Zn} in molten copper-zinc alloys from vapour pressures and boiling points.

Other Systems.—Several additional systems containing the volatile metals zinc and cadmium have been studied by similar methods. Fig. 6 gives the activity coefficients of these metals at 850° in solutions of copper, silver and gold, computed from the data of Schneider and Schmidt[10]

Dilute Solutions.—Henry's law states that in a dilute solution the activity of the solute is proportional to its concentration. It is evident that the concentration may be expressed in any convenient units since at sufficiently great dilution each concentration unit bears a fixed ratio to every other. Within the range of composition for which Henry's law is valid the activity coefficient is constant and its value is designated γ°. In Fig. 5, for example, γ°_{Zn} is 0·23.

It is frequently convenient and sometimes necessary to adopt a scale of activity which is independent of that of the pure substance. For example, if we are dealing with high-copper brasses and do not wish to

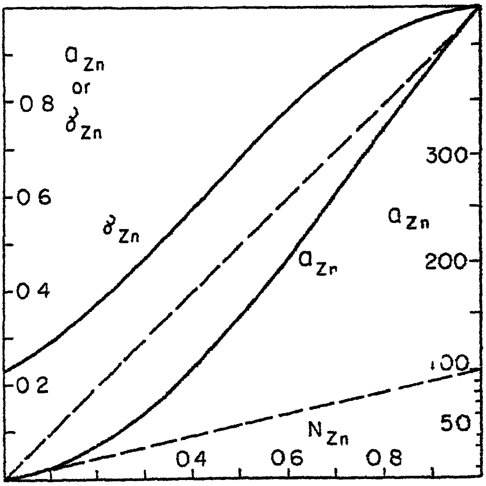

Fig. 5.—Activity and activity coefficient of zinc in molten brass at 1200° c. The activity scale along the right-hand margin is based upon the infinitely dilute solution.

concern ourselves with pure zinc, the latter would be an unnecessarily cumbersome standard reference state. In such a case it is convenient to select a standard state which lies within the composition range in which Henry's law is valid. It appears here that Henry's law is valid up to a mole fraction of about 0·05. A convenient reference state is secured by expressing the concentration in atom-% and taking $a = 1$ and $c = 1$ at 1 atom-%. There are many cases, however, in which Henry's law is valid only at extremely low concentrations and in general it is more satisfactory to define the standard state for dilute solutions by letting a/c approach unity as c approaches zero. The ratio a/c is an activity coefficient to which we shall give the symbol f, reserving the symbol γ for a coefficient based upon the pure component. The new scale of activity is shown along the right-hand margin of Fig. 5. It is based upon a hypothetical solution in which the activity (not necessarily the concentration) is unity and which in other respects has the properties of the infinitely dilute solution. This seems a complex definition but its use eliminates other complexities.

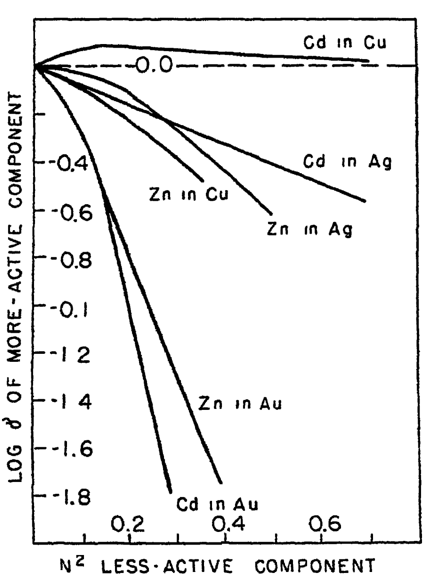

FIG. 6—Activity coefficient of the more volatile component in several liquid systems at 850° C.

The difference in chemical potential of zinc in the two standard states is the free energy decrease which occurs when 1 g.-atom of zinc is transferred from the pure liquid to the dilute solution of unit activity. The numerical value is obtained from eqn. (6) and the data of Fig. 5. The former may be written:

$$\mu^\circ_{Zn}\,(\text{dil. soln.}) - \mu^\circ_{Zn}\,(\text{pure}) = RT \ln \frac{a_{Zn}\,(\text{dil. soln.})}{a_{Zn}\,(\text{pure})} \quad . \quad . \quad (16)$$

in which the ratio of the activities of zinc in the two standard states is, of course, the same on either scale. At 1200° C., γ° is 0·23 and the ratio of the two activity scales is 0·0023. Hence the difference between the two standard chemical potentials is $RT \ln 0{\cdot}0023 = -17{,}800$ cal.

Activity from Electromotive Force Measurements

When an electrolytic cell operates reversibly its E.M.F. is related to the free energy change in the cell reaction by the equation

$$\Delta G = -nFE \,. \quad (17)$$

where F is the Faraday equivalent or 23,070 cal. per equivalent volt, E is the E.M.F. and n is the number

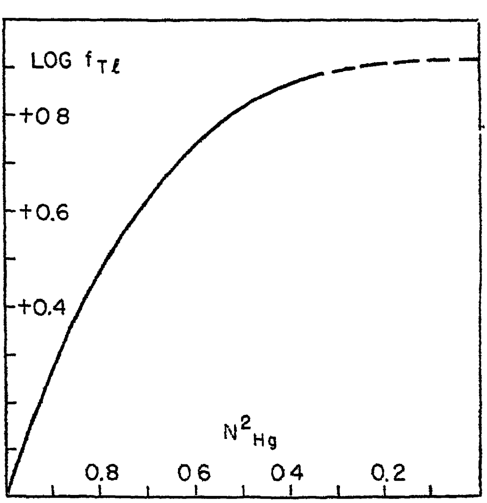

FIG. 7.—Activity coefficient of thallium in amalgams at 20° C.

of Faradays required for the cell reaction. When the electrodes are two alloys of the same metal but of different concentration and the electrolyte contains the ion of the more electropositive metal, the overall cell reaction is the transfer of this metal from one electrode to the other. In the classical experiments of Richards and Daniels[21] thallium amalgams of various concentrations were measured against a saturated amalgam in an aqueous solution of a thallous salt. The activity of thallium in the amalgam was then found by the equation

$$RT \ln \frac{a_2}{a'_2} = -nFE \quad . \quad (18)$$

The results have been discussed fully by Lewis and Randall[2] who used the infinitely dilute solution as the reference state making *a*/*N* for thallium equal to unity at infinite dilution. The activity coefficient at 20° is shown in Fig. 7. Here it should be noted the activity coefficient *f* measures the deviation from Henry's law which is positive and corresponds to negative deviation from Raoult's law. The semi-regular behaviour of this solution is clearly shown in the figure.

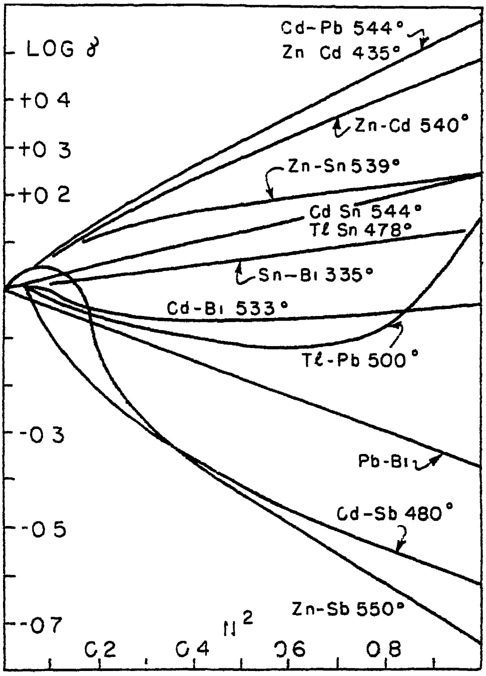

FIG. 8.—Activities of the more positive metal from electromotive force measurements in fused salt baths.

At higher temperatures fused salts are substituted for aqueous solutions. In this way Taylor[22] was able to determine the activities in several series of liquid alloys of zinc, cadmium, tin, lead and bismuth. The electrolyte must contain the ion of the more electropositive metal but it was found,

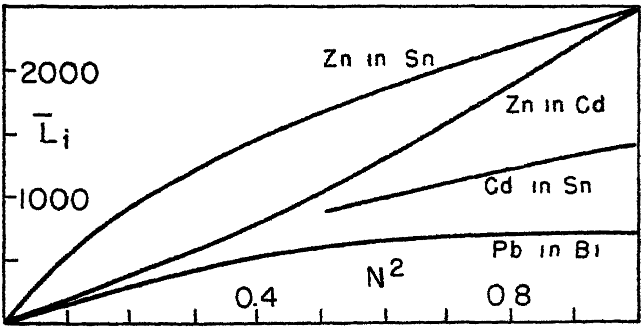

FIG. 9.—Partial molal heat of solution in several alloy systems.

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[21] Richards and Daniels, *J. Amer. Chem. Soc*, 1919, 41, 1732.

[22] Taylor, *J. Amer. Chem. Soc.*, 1923, 45, 2865

for example, that when pure zinc chloride was used in contact with zinc a metallic "fog" was formed. This was avoided by using a dilute solution of zinc chloride in a eutectic mixture of potassium and lithium chlorides. Taylor's results at temperatures near 500° C. are shown in Fig. 8. Similar results by Hildebrand and Sharma[23] and by Seltz[24] and his co-workers are included. It will be noted that many of the solutions are regular or semi-regular, but that in a few cases there is marked deviation from regularity in dilute solutions. This appears to be due to opposing tendencies among two components which, because of differences in internal pressure or atomic diameter, would be expected to show positive deviation from Raoult's law but on account of a tendency to form compounds actually show negative deviation over most of the range of composition.

Effect of Temperature on Regular Solutions

The activity coefficient changes with temperature in accordance with eqn. (11). By means of this equation the partial molal heat of solution $\bar{L}_1$ may be calculated when the activity coefficient is known as a function of temperature. The Helmholtz equation may also be used to calculate the heat of solution from the electromotive forces of the cells discussed above, when these are known at several temperatures. Thus

$$\bar{L}_1 = \bar{H}_1 - H_1^\circ = nF\,[T\,(\mathrm{d}E/\mathrm{d}T) - E] \qquad . \quad . \quad (19)$$

where $\bar{L}_1$ is the partial molal heat of solution of the more electropositive metal in the alloy. In regular solutions $\bar{L}_1$ is a linear function of N_2^2 while in semi-regular solutions the curves are not quite linear as illustrated from Taylor's data in Fig. 9.

Taylor found that in all of the cells he studied the heat of solution is practically independent of temperature within the limits of error of the experiments. Data on other semi-regular solutions confirm the conclusion that the heat of solution does not vary greatly with temperature. This conclusion should not be extended to systems which exhibit a strong tendency toward compound formation, and it is not to be regarded as at all precise even for strictly regular solutions.

By means of eqn. (12) the activity coefficient may be obtained from the heat of solution provided the solution is regular. This provision constitutes a serious limitation since in the usual experimental approach the activity coefficients must be determined before it is known whether or not the solution is regular. Nevertheless the equation affords a basis for rough estimates of activity coefficients which may be useful in a few special cases. It cannot be relied upon in the presence of a tendency toward compound formation. Thus Körber and Oelsen[25] used this method to estimate the activity coefficient of silicon in liquid iron from the heat of solution, resulting in entirely erroneous conclusions.

The temperature coefficient of the E.M.F. of a cell is directly related to the change in entropy in the cell reaction by the equation

$$\frac{\mathrm{d}E}{\mathrm{d}T} = \frac{\Delta S}{nF} \qquad . \quad . \quad . \quad . \quad . \quad (20)$$

When the cell is of the type under discussion the entropy change is that of transfer of 1 g.-atom of the electropositive metal from the pure metal to the molten alloy, a value which for regular solutions is given by eqn. (10), for semi-regular solutions by (14). It follows that for such a cell

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[23] Hildebrand and Sharma, *J. Amer. Chem. Soc.*, 1929, **51**, 462.

[24] (*a*) Seltz and Dewitt, *J. Amer. Chem. Soc.*, 1938, **60**, 1305; (*b*) Strickler and Seltz, *J. Amer. Chem. Soc.*, 1936, **58**, 2084; (*c*) Seltz and Dunkerley, *J. Amer. Chem. Soc.*, 1942, **64**, 1392; (*d*) Seltz, *Trans. Electrochem. Soc.*, 1940, **77**, 233.

[25] Körber and Oelsen, *Mitt. Kaiser Wilhelm Inst. Eisenforsch.*, 1936, **18**, 109.

$$nF\frac{dE}{dT} = -DR \ln N_1 \quad . \quad . \quad . \quad . \quad . \quad (21)$$

in which the value of D is unity for regular solutions. Values of dE/dT for a number of cells studied by Taylor,[22] Hildebrand and Sharma[23] and by Seltz and co-workers[24] are plotted against the logarithm of the mole fraction in Fig. 10. It is noted that the value of D lies between the limits 0·95 and 1·5 for those solutions which appear to be semi-regular and varies strongly at compositions corresponding to solid compounds.

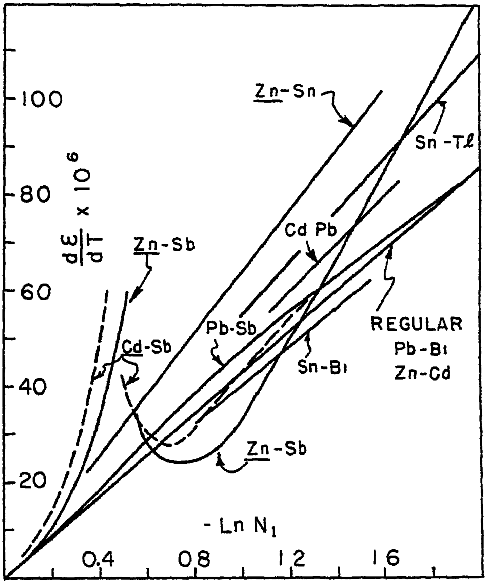

Fig. 10.—Temperature coefficient of electromotive force in the formation of molten alloys.

Activity from Phase Diagrams

For certain kinds of binary phase diagrams it is possible to determine activity coefficients in the liquid solutions from the location of the solidus and liquidus lines. The reverse procedure of utilising activities determined by E.M.F. measurements to establish the phase boundaries is illustrated in the work of Strickler and Seltz[24b] on the system lead-bismuth. The calculation of activity from the phase diagram is limited to systems in which the activities in the terminal solid solutions are known or in which these solutions cover only a very limited range of composition. Moreover, if intermetallic compounds are formed they interfere seriously with the attempt to extend the calculations over the entire composition range. For systems of the simple eutectic type the method affords a means of obtaining coefficients of at least approximate validity. The method depends upon two principles, (1) that for liquid and solid phases in equilibrium the chemical potentials are the same in both phases, and (2) that the difference in chemical potential (free energy) between the liquid and solid states of the pure metal is calculable from the heat of fusion. The calculation will be illustrated for two solutions in liquid iron.

The Systems Iron-Sulphur and Iron-Copper.—The heat of fusion of iron is 3670 cal. per g.-atom at the melting point 1535°. The liquid has a slightly higher heat capacity than the solid, ΔC_p being about 0·3 cal./degree.[26] From these data the change in free energy on melting is

$$\text{Fe}\ (\delta) = \text{Fe (liquid)}\ ;\ \Delta G^\circ = 3130 - 0{\cdot}3\,T \ln T + 0{\cdot}518T \quad . \quad (22)$$

Values of $(G\ (\text{liquid}) - G\ (\delta))/T$ are shown in Table II. When γ-iron is the solid phase a slight correction is required and the resulting values are also tabulated. Since the undercooled pure liquid is taken as the standard state, the activity of the solid is less than unity and its value may be obtained from the free energy by eqn. (6). Values of log a for δ- and γ-iron are included in Table II. It is evident that when a liquid solution is in equilibrium with substantially pure iron, the activity of iron in the melt is that given in the table.

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[26] Darken and Smith, private communication.

TABLE II

FREE ENERGY AND ACTIVITY OF SOLID IRON RELATIVE TO LIQUID

$T°$ K.	$\frac{G_l - G_\delta}{T}$	$\frac{G_l - G_\gamma}{T}$	$-\log a_\delta$	$-\log a_\gamma$
1183	1·019	1·019	0·223	0·223
1300	0·760	0·771	0·166	0·168
1308	0·744	0·755	0·162	0·165
1400	0·571	0·584	0·125	0·127
1500	0·404	0·415	0·088	0·091
1600	0·258	0·264	0·056	0·057
1673	0·162	0·162	0·035	0·035
1700	0·128	0·126	0·028	0·026
1808	0·000		0·000	0·000

The phase diagram for the system iron-sulphur [27] is reproduced in Fig. 11 The portion up to 36·5 % sulphur may be regarded as a binary Fe — FeS in which there is essentially no solubility in the solid iron and considerable positive deviation from Raoult's law in the liquid. In Table III the first two columns are taken directly from the diagram and the third from Table II. The fourth contains the mole fraction of Fe when the remainder is figured as FeS. The fifth gives the value of log γ_{Fe} at the liquidus temperature. So far no assumptions are involved but when we wish to obtain activity coefficients at temperatures other than the liquidus the necessary data are lacking. The nearest approximation is the assumption that b of eqn. (15) is independent of temperature, or that log γ_{Fe} varies inversely with T. In this way the last three columns are

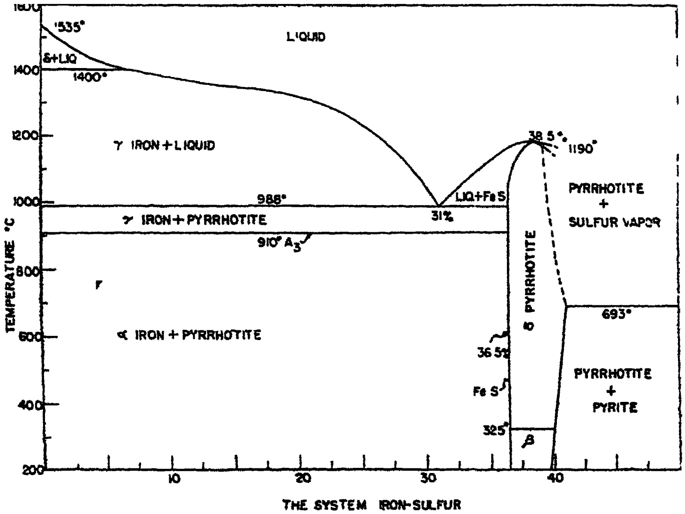

FIG. 11.—Phase diagram of the system iron-sulphur.

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[27] *Metals Handbook* (Amer. Soc. Metals, Cleveland, 1948).

filled. The data for 1600° are shown in Fig 12 plotted against the square of the mole fraction of FeS and extrapolated to a hypothetical pure liquid FeS. It should be pointed out that the calculation does not assume the existence of FeS molecules. The formula FeS is merely assigned to one of the components for ease of calculation.

TABLE III

ACTIVITY OF IRON IN LIQUID SOLUTIONS FE – FES

Temperature ° C.	Sulphur %	log a_{Fe}	N_{Fe}	log γ_{Fe}			
				t	1500	1600	1700
1535	0		1·000	0·000			
1400	6·9	—0·035	0·870	0·025	0·024	0·022	0·021
1350	15·0	—0·050	0·693	0·109	0·100	0·094	0·090
1300	22·0	—0·066	0·508	0·228	0·200	0·191	0·182
1200	26·4	—0·099	0·374	0·328	0·272	0·258	0·245
1100	29·1	—0·138	0·284	0·409	0·317	0·300	0·285
988	31·0	—0·185	0·216	0·481	0·343	0·324	0·308
Extrap.	36·5		0·0		0·433	0·410	0·390

The system iron-copper is very similar to iron-iron sulphide. Solid iron, however, dissolves some 5 to 10 % copper and its activity must be slightly lowered thereby. In the following calculations an activity of 0·95 is arbitrarily assigned to iron in the saturated solid solution. In Table IV the first two columns show the liquidus curve as read from Hansen's [28] phase diagram. The third gives the activity of pure solid iron from Table II and the fourth the activity at the liquidus obtained by adding log 0·95 to the preceding column. The logarithm of the activity coefficient at the liquidus temperature is shown in the fifth column and from this the value of b of eqn. (15) is computed to give the sixth column. It is noted that b undergoes considerable variation along the liquidus line ; it would be useful to know how much of this is due to temperature and how much to composition. For the present it is assumed that b is a function of composition only and on this basis the values of log γ_{Fe} at 1,600° are calculated from smoothed values of b. The last column contains values of log γ_{Cu} obtained by integration of the Gibbs-Duhem equation which will be discussed in the following section. The results are shown graphically in Fig. 13.

TABLE IV

ACTIVITY OF IRON IN LIQUID IRON-COPPER SOLUTION

Temp. ° C.	Copper mol. fr.	log a_{Fe} (pure solid)	log a_{Fe} (solution)	log γ_{Fe} at t ° C.	b	log γ_{Fe} at 1,600	log γ_{Cu} at 1600
1528	0·00	—0·000	0·000		(12,400)	0·000	1·08
1477	0·12	—0·015	0·037	0·019	10,500	0·013	0·77
1460	0·20	—0·020	0·042	0·055	10,900	0·048	0·59
1440	0·40	—0·025	0·047	0·175	8,500	0·162	0·32
1430	0·60	—0·028	0·050	0·348	7,500	0·315	0·16
1390	0·80	—0·038	0·060	0·639	7,600	0·568	0·06
1320	0·90	—0·059	0·081	0·919	8,300	0·784	0·02
1094	0·97	—0·141	0·163	1·36	9,100	1·00	0·00
Extrap.	1·00				(9,600)	1·120	0·00

The System FeS-FeO.—The system composed of the oxide and sulphide of iron is of interest in connection with the activity of each of these substances when dissolved in molten iron. According to Oberhofer[29] this is a simple eutectic system with the eutectic at 42 % FeO and 940° c. The melting points of the components according to the same source and the heats of fusion according to Kelley[30] are: FeS, 1189° and 5000 cal.; FeO 1388° and 7700 cal. These are rough data but from them it may be calculated, assuming a regular solution, that the value of *b* for FeS is 2900 cal. and for FeO is zero. If the solution is actually regular the value of *b* should be the same for both components which indeed would have been the result if the eutectic composition had been taken as about 44 % FeO. As an average value for *b* we may take 1500 cal. for both components. This means that the solution is nearly ideal, but in very dilute solutions the deviation is enough to be significant. For the activity coefficient of either component in very dilute solution in the other we find the following values of γ_0: at 1500°, 1·53; at 1600°, 1·50; at 1700°, 1·47. These will be used in a later section.

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[28] Hansen, *Der Aufbau der Zweistofflegierungen* (J. Springer, Berlin, 1936).

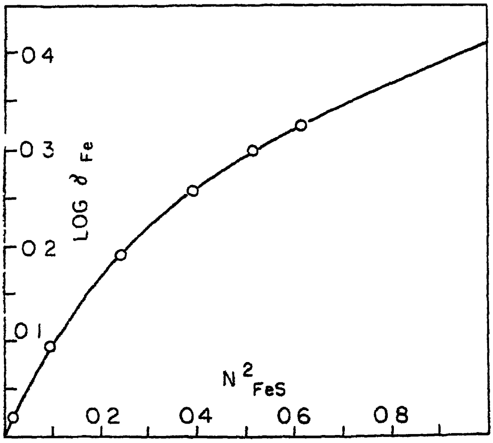

FIG. 12.—Activity coefficient of iron in Fe-FeS solutions at 1600° c.

The System Lead-Silver.—Another example is found in the recent calculations of Chou and Elliott[31] for the system lead-silver. The phase diagram which has been well established by several closely agreeing researches[28] is shown in Fig 14. On the silver side the solubility in the solid is negligible and the liquidus line follows the expected behaviour for an ideal solution up to an atom fraction of lead of about 0·20. The free energy of solid silver compared to that of the liquid may be found from the heat of fusion and heat capacities given by Kelley[30]

$$\text{Ag}\ (l) = \text{Ag}\ (s)\ ;$$
$$\Delta G^\circ = -694 + 5{\cdot}99T \log T - 7{\cdot}5 \times 10^4 T^{-2} - 17{\cdot}0T$$

and from this the activity of solid silver and hence that of silver in the equilibrium liquid may be found at each temperature. Following the same procedure that was used for iron-copper, the activities of silver and lead have been computed at 1000° and are shown in Fig. 15. This proves to be a case in which the solution is nearly regular and the activity diagram nearly symmetrical.

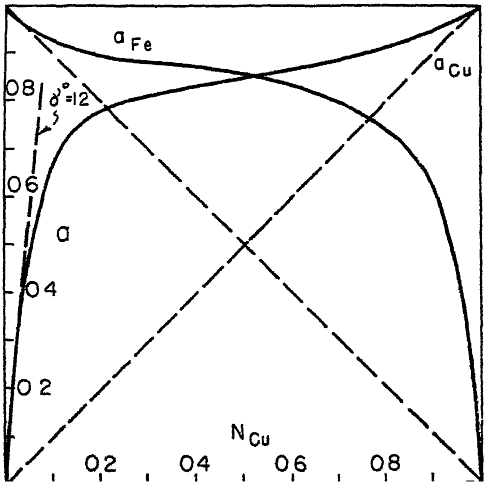

FIG. 13.—Activities of the components in the system Fe-Cu at 1600° c.

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[29] Oberhoffer, *Das Technische Eisen.* (J. Springer, Berlin, 1925), p. 93.
[30] Kelley, *U.S. Bur. Mines Bull.* No. 371 (1934) and No. 393 (1936).
[31] Chou and Elliott, unpublished.

The System Iron-Silicon containing an Intermetallic Compound.—When the two components form an intermetallic compound having a congruent melting point the activities in the liquid phase at compositions near that of the compound may be calculated by a method proposed by Hauffe and Wagner.[32] This method applies the principles discussed above to the determination of the chemical potential of either component from its effect on the melting point of the compound. For the difference in chemical potential of component 2 between the compound of mole fraction X_2 and the equilibrium liquid of mole fraction N_2, Hauffe and Wagner derived the formula

$$\Delta\mu_2 = \frac{\Delta H_f}{\theta}\left(\frac{N_1\,\Delta T}{N_2 - X_2} + X_1\int_{X_2}^{N_2}\frac{\Delta T}{(N_2 - X_2)^2}\,\mathrm{d}N_2\right) \quad . \quad (23)$$

where ΔH_f is the heat of fusion per formula weight and θ the absolute melting point of the compound and ΔT is the melting point lowering corresponding to the concentration difference $N_2 - X_2$

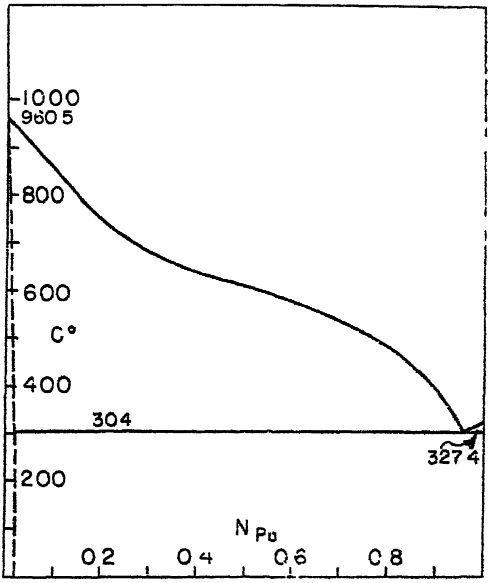

FIG. 14.—Phase diagram of the system lead-silver.

The researches of Haughton and Becker[33] have established the liquidus curve on both sides of the compound FeSi. From their data and the value $\Delta H_f/\theta = 3{\cdot}5$ suggested by Hauffe and Wagner, it is possible with the aid of eqn. (22) to obtain values of $\Delta\mu$ for silicon and iron in the liquid alloys in the range 20 to 50 % silicon. These values alone are not sufficient to establish the activities relative to the pure components. They do, however, determine relative activities within the stated composition range and hence a series of values for $\log \gamma +$ a constant* within this range. Evaluation of the constant is not difficult in the present case.

The melting point of silicon is lowered from 1414° to 1207° in contact with a melt of 0·27 mole fraction iron. Taking the heat of fusion reported by Körber and Oelsen[25] of 11,100 cal. per g.-atom, the activity coefficient of silicon in the melt is found to be 0·865. This corresponds to a value of *b* (eqn. (15)) of —5800 cal., and assuming this constant, the activity coefficient at 1600° and $N_{Fe} = 0{\cdot}27$ becomes 0·89. This is plotted as point A in Fig. 16.

A very short extrapolation to the point B is sufficient to establish the activity coefficient at a composition corresponding to the high silicon extremity of the range of values based upon the compound FeSi and thus to fix the value of the constant. This series of values is then used to extend the curve to the point C. Extrapolation beyond this point would involve considerable uncertainty, but this is unnecessary since the point *D* is independently determined from equilibrium data on the deoxidation of steel with silicon. This point will be discussed along with other activities based on chemical equilibrium in a later section.

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[32] Hauffe and Wagner, *Z. Elektrochem.*, 1940, **46**, 160.
[33] Haughton and Becker, *J. Iron Steel Inst.*, 1930, 121, 315.

* The writer is indebted to J. F. Elliott for this and other calculations.

Activity of the Second Component in a Binary System

The Gibbs-Duhem Equation.—When the activity of one component of a binary solution is known over a range of compositions the variation in activity of the second is given by the Gibbs-Duhem equation :[34]

$$N_1 \, d \ln a_1 + N_2 \, d \ln a_2 = 0 \quad . \quad . \quad . \quad (24)$$

If the range of concentrations in which a_2 is known extends to $N_2 = 0$, the equation may be integrated with this as one of the limits, to yield values a_1 extending to the pure component. It is generally a little more convenient to use activity coefficients and the following integrated form is readily derived from the foregoing equation :

$$\log \gamma_1 = - \int_0^{\gamma_2} \frac{N_2}{N_1} \, d \log \gamma_2 \quad . \quad . \quad . \quad . \quad (25)$$

As an example of the use of this equation we shall obtain the activity coefficients of FeS in Fe at 1600° from the data of Table III.

In Fig. 17 the molar ratio N_{Fe}/N_{FeS} is plotted as ordinate against the logarithm of the activity of iron at 1600° from Table III. The integration is carried out graphically in the steps indicated in the figure, with the results shown in Table V. Graphical integration suffices for all steps except the last which extends to a molar ratio of infinity and therefore cannot be evaluated graphically. The assumption that the solution is semi-regular provides the basis for solving this step. For such a system the value of b in eqn. (15) is linear in N_1 over a sufficient range and in this case may be represented by $b = 12{,}800 - 13{,}600 \, N_{FeS}$, from which $\log \gamma_{Fe} = 1{\cdot}49 \, N^2_{FeS} - 1{\cdot}59 \, N^3_{FeS}$. Substitution of this value for $\log \gamma_2$ in eqn. (25) and its solution for the interval beyond G yields the value shown in the table. Similar integrations were carried out for the data at 1500° and 1700°. For these two temperatures the resulting values of the activity coefficient of FeS are shown in the last two columns of Table V. It is now possible to construct a complete activity-composition diagram for the system Fe-FeS at 1600° and this is done in Fig. 18.

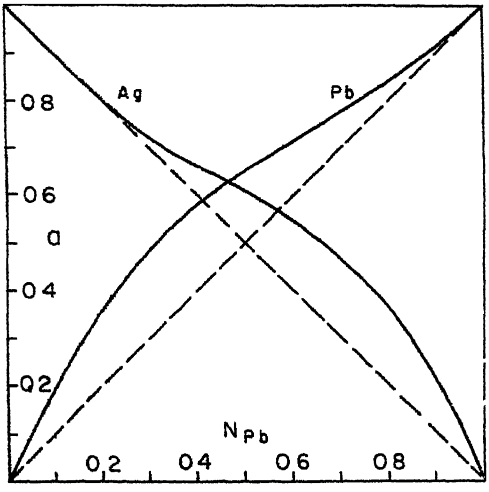

FIG. 15.—Activities in lead-silver solutions at 1000°.

Regular Solutions and the Duhem Equation.—A corollary of the Duhem equation which is especially useful in regular and semi-regular solutions is the equation *

$$\frac{d \log \gamma_1}{d \, (N_2^2)} = \frac{d \log \gamma_2}{d \, (N_1^2)} \quad . \quad . \quad . \quad . \quad . \quad (26)$$

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[34] Glasstone, *Thermodynamics for Chemists* (D. Van Nostrand, New York, 1947 p. 368 ; also Ref. 2, p. 268.

* To derive (26) differentiate (25) with respect to N^2 and use the relations $d(N_2^2) = 2 \, N_2 dN_2 = - \, 2N_2 dN_1$ to obtain $d \log \gamma_1 / d(N_2^2) = (N_2/N_1) \, d \log \gamma_2 dN_1$ which simplifies to (26).

TABLE V

INTEGRATION OF GIBBS-DUHEM EQUATION FOR FE-FES AT 1600° C.

N_{Fe}/N_{FeS}	Step (Fig. 16)	Area	log γ_{FeS}	γ_{FeS}	N_{FeS}	a_{FeS}	γ_{FeS}	
							1500°	1700°
0·0			0·00	1·00	1·0	1·00	1·00	1·00
0·2	AB	0·003	0·003	1·01	0·833	0·84	1·01	1·01
0·5	BC	0·025	0·028	1·07	0·667	0·71	1·07	1·06
1·0	CD	0·057	0·085	1·22	0·50	0·61	1·23	1·20
2·0	DE	0·126	0·211	1·62	0·333	0·54	1·65	1·58
4·0	EF	0·178	0·389	2·4	0·200	0·49	2·5	2·3
6·67	FG	0·113	0·502	3·18	0·130	0·41	3·5	3·0
∞	G∞	0·344	0·846	7·0	0·000	0·00	8·1	6·3

From this it is evident that in any solution if one component conforms to eqn. (15) the other must also conform. Further in a regular solution the value of b is the same for both components Regular solutions are therefore entirely symmetrical with respect to activities of the two components. An excellent example of a system which behaves in this manner is the tin-thallium system studied by Hildebrand and Sharma.[23] Their activity curves at three temperatures are reproduced in Fig 19.

In semi-regular solutions the value of b may be constant only under limiting conditions of the very dilute solution Using a simplified form of (15) in which $\beta = b/2{\cdot}303\ RT$, we may write for the activity coefficient of each component in dilute solution

$$\log \gamma_1 = \beta_1 N_2^2 \text{ and}$$
$$\log \gamma_2 = \beta_2 N_1^2 \quad . \quad (27)$$

The shapes of the log γ against N^2 curves for a semi-regular solution in which $\beta_1 > \beta_2$ are shown schematically in Fig. 20. The slopes of the two curves are prescribed throughout by eqn. (26), which provides also a simplified solution of the Duhem equation within the linear portion of either curve. A slightly more complex case in which β is expressed as a function of N has already been illustrated for the case of FeS in Fe.

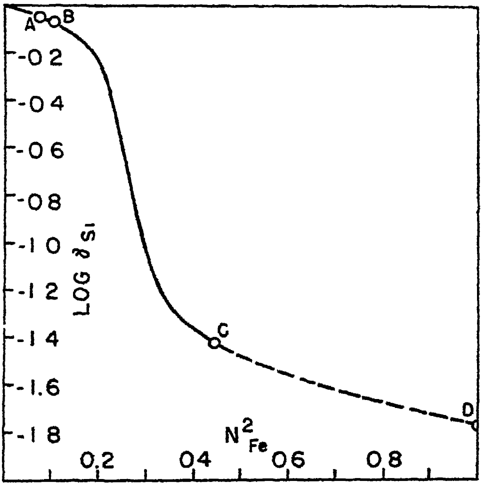

FIG. 16.—Activity coefficient of silicon in Fe-Si alloys at 1600° C.

Activity from Distribution Equilibrium

When a solute is distributed between two immiscible solvents the state of equilibrium at constant temperature is characterised by a constant ratio of its activity in one phase to that in the other. If its activity in each phase is referred to the same state of the pure solute, then the ratio becomes unity and the activity of the solute is the same in both phases. When the activity in one phase is known that in the other phase is established, and the activity coefficient is obtainable from the distribution ratio.

The System Silver-Aluminium.—Chou and Elliott[31] have employed this principle to determine the activity of silver in molten silver-aluminium alloys. The distribution of silver between the nearly immiscible liquids aluminium and lead was studied by Lorenz and Erbe[35] at temperatures of 750° and 1000° c. The activity of silver in the lead layer is known from Fig. 15 hence that in the contiguous aluminium layer is also known. The activity of silver computed in this manner is shown in Fig 21 That of aluminium in the same alloys, found by integration of the Gibbs-Duhem eqn. (25) is also shown.

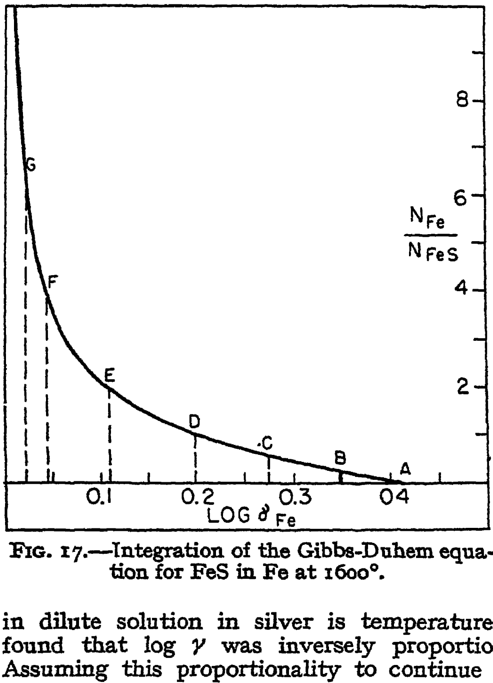

FIG. 17.—Integration of the Gibbs-Duhem equation for FeS in Fe at 1600°.

Aluminium in Liquid Iron.—The distribution of aluminium between molten iron and silver at 1600° was studied by the writer[36] who found a constant distribution ratio at concentrations up to a mole fraction of about 0·18 in the iron layer. The ratio of the mole fractions N_{Al} (in Ag)/N_{Al} (in Fe) was 0·68 and hence the ratio γ_{Al} (in Fe)/γ_{Al} (in Ag) = 0·68. The activity coefficient of aluminium in dilute solution in silver is temperature-dependent and Chou and Elliott found that log γ was inversely proportional to the absolute temperature Assuming this proportionality to continue the value of γ°_{Al} (in Ag) at 1600° is 0·037. Accordingly γ°_{Al} (in Fe) is 0·025.

Sulphur in Liquid Iron.—Bardenheuer and Geller[37] determined the distribution ratio for sulphur between liquid iron and slags of approximately the composition FeO. They summarised their results in the expressions:

$$L = \%S\ (\text{slag})/\%S\ (\text{metal});$$
$$\log L = 2390/T - 0{\cdot}714.$$

This equation, which is in excellent agreement with similar results of Fetters and Chipman,[38] may be used along with other data to find the activity coefficient of iron sulphide in dilute solutions in liquid iron. Values of L at three temperatures are given in Table VI. The corresponding ratio of mole fractions of FeS in the two layers is also shown. It will be remembered that the activity of FeS in dilute

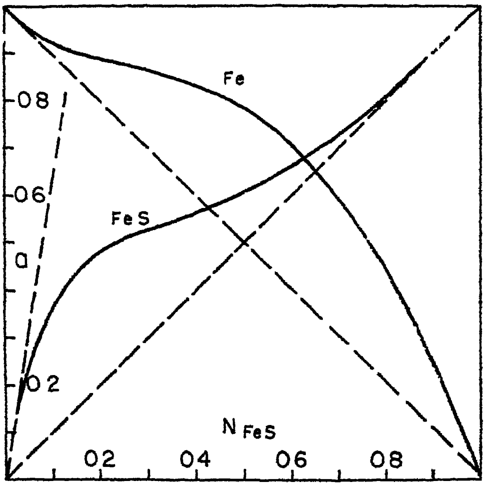

FIG. 18.—Activities in the system Fe-FeS at 1600° c. $\gamma^{\circ} = 7{\cdot}0$.

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[35] Lorenz and Erbe, *Z. anorg. Chem.*, 1929, **183**, 311.
[36] Chipman, *Trans. Amer. Soc. Met.*, 1934, **22**, 885.
[37] Bardenheuer and Geller, *Mitt. Kaiser Wilhelm Inst. Eisenforsch.*, 1934, **16**, 77.
[38] Fetters and Chipman, *Trans. Amer. Inst. Min. Met. Eng.*, 1941, **145**, 95.

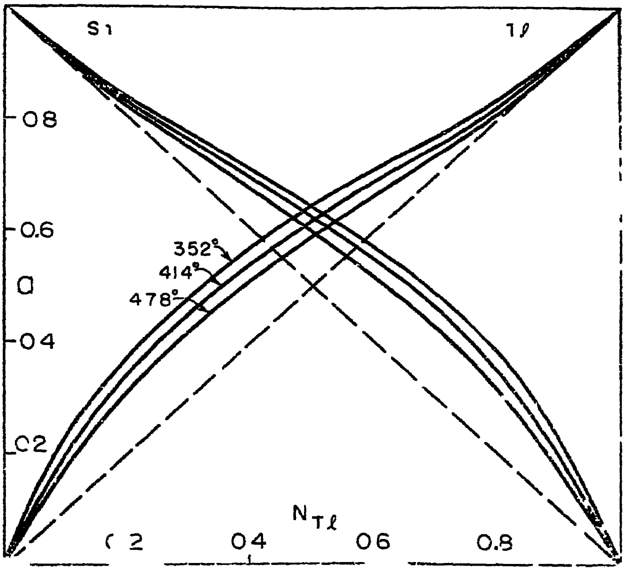

FIG. 19.—Activities in the system tin-thallium at three temperatures.

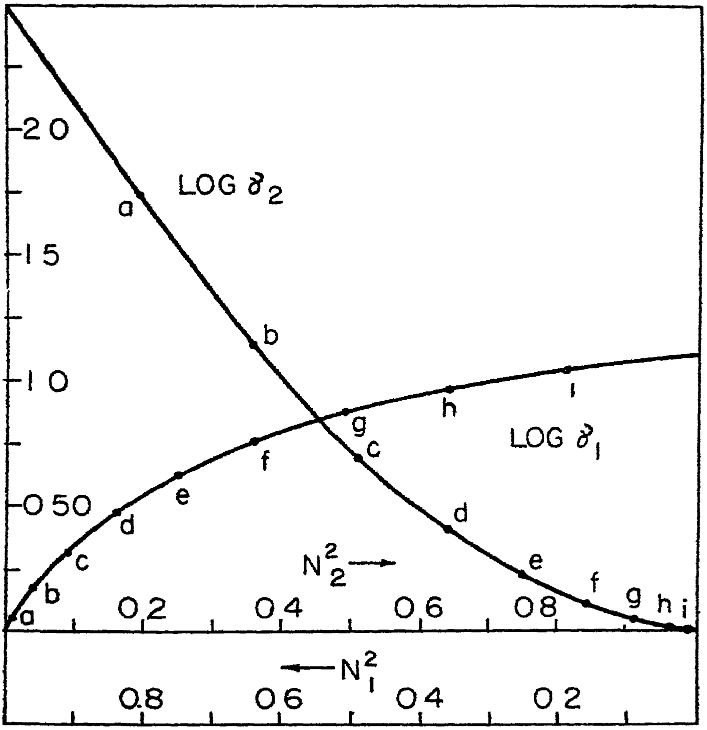

FIG. 20.—Activity coefficients of two components in a semi-regular solution. The slopes of the two curves at *a*, *a*, etc., are equal.

solutions in FeO has been obtained from the phase diagram in an earlier section. These values are repeated in the table. The product of γ°_{FeS} (in FeO) and the molar distribution ratio yields γ°_{FeS} (in Fe). The corresponding values obtained from the iron-sulphur phase diagram are recorded in the last line of Table VI and it will be noted that the agreement is excellent.

TABLE VI

ACTIVITY COEFFICIENT OF FeS IN Fe (DILUTE SOLUTION)

Temperature, ° c.	1500	1600	1700
$L = (\%S)/[\%S]$	4·30	3·64	3·15
N_{FeS} (slag)/N_{FeS} (metal)	5·53	4·69	4·05
γ°_{FeS} (in FeO)	1·53	1·50	1·47
γ°_{FeS} (in Fe)	8·5	7·0	6·0
γ°_{FeS} (in Fe) (from phase diagram)	8·1	7·0	6·3

Ferrous Oxide in Slags.—The same principle has been utilised to determine the activity of FeO in slags of the types used in steelmaking.[38] The solubility of FeO, of as high purity as can be made, in liquid iron at 1600° is equivalent to 0·23 % oxygen in the metal. This is taken as the standard reference state and assigned unit activity. The activity of FeO in another slag is established by the concentration of oxygen which it is capable of imparting to the metal, at the same temperature, divided by 0·23. The activity of FeO in slags consisting of FeO, SiO_2, CaO and MgO is shown in Fig. 22 which is reproduced from the work of Taylor and Chipman.[39] Any further discussion of activities in slags would carry us too far from the subject of this paper. The data for ferrous oxide are cited as one example of a method which has great potential usefulness in process metallurgy.

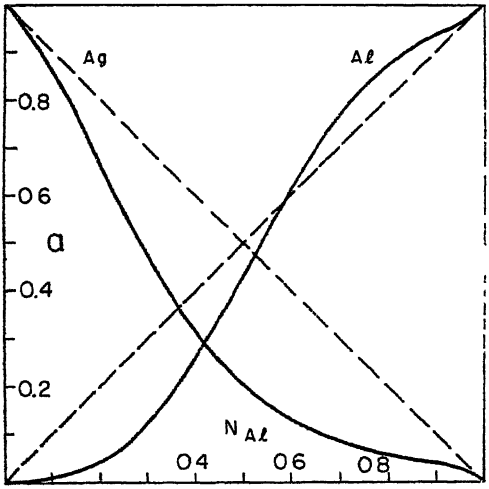

FIG. 21 —Activities in the system silver-aluminium at 1000°.

Activity from Chemical Equilibrium

Carbon in Liquid Iron.—In any chemical equilibrium in which the activity of every participant but one is independently known, a series of equilibrium determinations over a range of concentrations serves to fix the activity of that component. Thus the activity of carbon in austenite as well as in molten iron-carbon alloys has been established through studies of the reaction:

$$\mathrm{C\ (in\ Fe)} + \mathrm{CO_2} = 2\,\mathrm{CO}\ ;\ K = p^2_{CO} / (p_{CO_2} \cdot a_C).$$

In his very careful study of this equilibrium in austenite, Smith[40] has arrived at accurate values for the activity of carbon at 800° and 1000° C. He plotted the function log $(p^2_{CO} / p_{CO_2} \cdot n_1/n_2)$ against n_2/n_1 and obtained a straight line relationship up to an atom ratio of carbon to iron, n_2/n_1 of 0·07.

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[39] Taylor and Chipman, *Trans. Amer. Inst. Min. Met. Eng.*, 1943, **154**, 228.
[40] Smith, *J. Amer. Chem. Soc.*, 1946, **68**, 1163.

The available data on the same reaction in liquid iron may be treated in the same manner as shown in Fig. 23 which is based on the data of Marshall and Chipman [41] at 1540° c. Here the data obtained at a total pressure

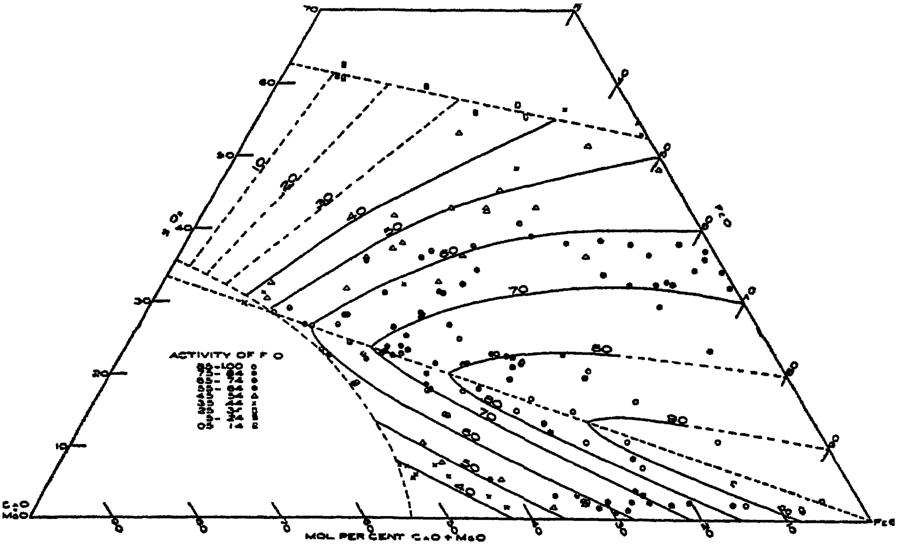

FIG. 22 —Activity of FeO in slags of CaO-MgO-SiO$_2$-FeO.

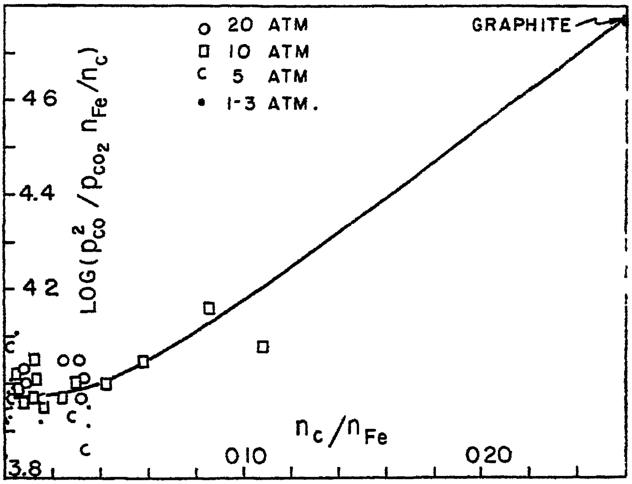

FIG. 23.—Computation of activity of carbon in iron at 1540°.

of 10 atm. appear to form the most dependable series and these are fitted by a line of slight curvature which extends upward to a point corresponding to saturation of the iron with graphite. The gas composition for this point is taken from the free energy compilation of Wagman, Rossini and their collaborators.[42] The activity of carbon in the melt is proportional to p^2_{CO}/p_{CO_2} and the proportionality factor may be determined on either of two scales of measurement. The results on both scales are shown in Table VII. If the standard state for carbon be taken as pure graphite the resultant values of the activity are shown in the fourth column. A more convenient measure is given in the fifth column in which the activity of carbon is taken as equal to its percentage in a solution of infinite dilution. Values for the activity coefficient $f_C = a_C/\%C$ are contained in the sixth column while the seventh gives the activity of iron calculated from the preceding columns through integration of the Gibbs-Duhem equation. It should be noted that while values in the fourth column apply only at 1540°, those of the last three columns are probably not very sensitive to changes in temperature.

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[41] Marshall and Chipman, *Trans. Amer Soc. Met*, 1942, 30, 695.

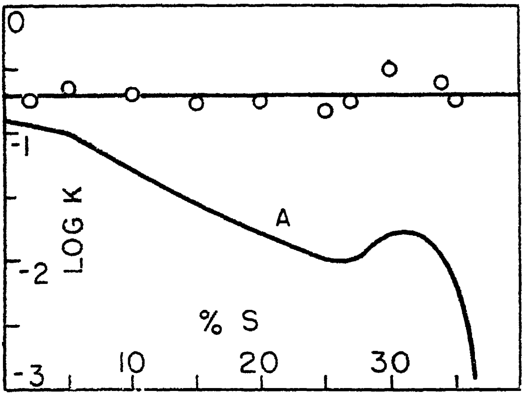

FIG. 24.—Equilibrium constant in the reaction $FeS + H_2 = Fe + H_2S$ at 1475°; line A, Maurer; circles, recalculated on basis of activities.

TABLE VII

ACTIVITY OF CARBON IN MOLTEN IRON AT 1540°

Concentration		$\frac{p^2_{CO}}{p_{CO_2}}$	Activity of C		$f_C = a_C/\%\ C$	a_{Fe}
% C	r_C/n_{Fe}		graphite = 1	$a_C = \%\ C$ at low C		
0·000	0·000				1·00	1·00
0·216	0·01	93	0·0061	0·216	1·00	
0·425	0·02	191	0·0125	0·443	1·04	
0·64	0·03	292	0·0191	0·68	1·06	
0·85	0·04	400	0·0261	0·93	1·10	0·96
1·06	0·05	525	0·0343	1·23	1·16	
1·28	0·06	670	0·0438	1·57	1·23	0·93
1·68	0·08	1,030	0·0673	2·40	1·43	0·91
2·10	0·10	1,510	0·0988	3·53	1·68	0·88
2·50	0·12	2,130	0·139	4·97	1·98	0·85
2·92	0·14	2,930	0·191	6·84	2·34	0·81
4·12	0·20	7,200	0·470	16·8	4·08	0·70
5·20	0·26	15,300	1·00	35·8	6·88	0·59

Oxygen in Molten Iron.—The equilibria of oxygen in molten iron with the gas mixtures H_2O-H_2 and CO_2-CO have been studied by several investigators.[41] [43] In each case the ratio $p_{H_2O}/(p_{H_2}\cdot\%\ O)$, or $p_{CO_2}/p_{CO}\cdot\%\ O)$ has been found to be constant at constant temperature up to the limit of solubility in the melt. This is sufficient evidence to enable us to write $a_O = \%\ O$ at all concentrations up to saturation in simple iron-oxygen alloys. The effect of a third component will be mentioned later.

[42] Wagman, Kilpatrick, Taylor, Pitzer and Rossini, *Nat. Bur. Stand. J. Res.*, 1945, **34**, 143.

[43] Fontana and Chipman, *Trans. Amer. Soc. Met.*, 1936, **24**, 313.

Sulphur in Molten Iron.—The equilibrium of sulphur in liquid iron with gaseous mixtures of hydrogen and hydrogen sulphide was studied by Chipman and Li [44] and by White and Skelly.[45] In these researches it was found that the ratio $p_{H_2S}/(p_{H_2} \cdot \%\ S)$ was constant up to 1·2 % sulphur or higher.

The work of Maurer, Hammer and Mobius [46] covered a much wider range, extending to 36·5 %, the theoretical composition of FeS. These investigators confirmed the proportionality of activity to composition at low concentrations but reported large deviations from ideal behaviour in concentrated solutions.

We have already derived values for the activities of FeS and Fe from the phase diagram and have shown that these are in agreement with calculations based on distribution. It may also be shown that they are in agreement with the results of Maurer, Hammer and Möbius. In Fig. 24, curve A is a reproduction of their plot for log K at 1475° C., where $K = (p_{H_2S}/p_{H_2})(N_{Fe}/N_{FeS})$. Using our new values for the activity coefficients at 1,500°, values of the thermodynamic equilibrium constant are found by multiplying Maurer's K by γ_{Fe}/γ_{FeS}. Values so obtained are also shown in the figure, from which it is evident that the results over the range 0–35 % S are adequately represented by a single value of log $K = -0{\cdot}70$.

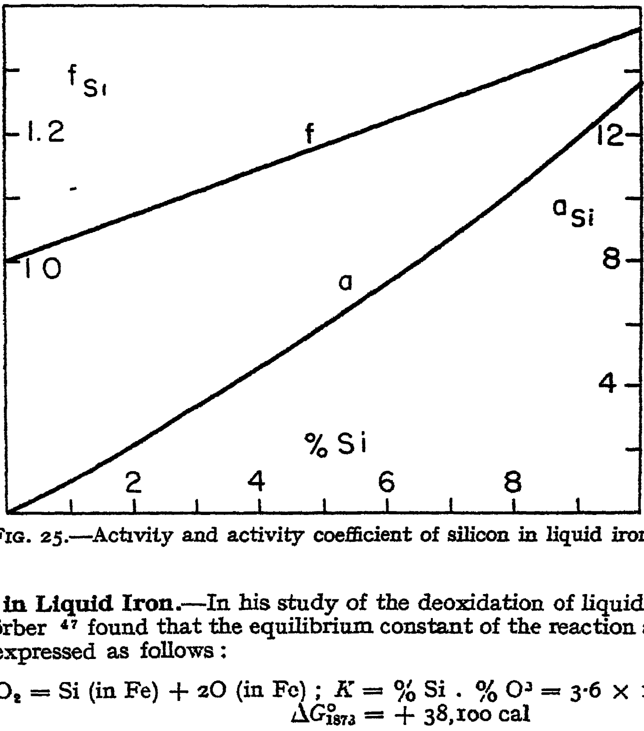

FIG. 25.—Activity and activity coefficient of silicon in liquid iron.

Silicon in Liquid Iron.—In his study of the deoxidation of liquid steel with silicon, Körber [47] found that the equilibrium constant of the reaction at 1600° C. could be expressed as follows:

$$(a)\ SiO_2 = Si\ (\text{in Fe}) + 2O\ (\text{in Fe})\ ;\ K = \%\ Si \cdot \%\ O^2 = 3{\cdot}6 \times 10^{-5}$$
$$\Delta G^\circ_{1873} = +\ 38{,}100\ \text{cal}$$

The free energy of formation of SiO_2 from its elements at 1600° is calculable from its heat of formation and the known entropies and heat capacities of each substance concerned, on the basis of the third law of thermodynamics. The result is:

$$(b)\ Si\ (\text{liquid}) + O_2\ (\text{gas}) = SiO_2\ (\text{solid})\ ;\ \Delta G^\circ_{1873} = -126{,}300\ \text{cal.}$$

[44] Chipman and Li, *Trans. Amer. Soc. Met.*, 1937, **25**, 435.

[45] White and Skelly, *J. Iron Steel Inst.*, 1947, **155**, 201.

[46] Maurer, Hammer and Möbius, *Arch. Eisenhüttenw.*, 1942, **16**, 159.

[47] Körber, *Stahl Eisen*, 1934, **54**, 535.

From equilibrium studies of the reactions of oxidising gases with liquid iron, the writer [48] has found the following value for the solution of oxygen in liquid iron:

(*c*) O_2 (gas) = 2O (in Fe) ; $\Delta G^\circ_{1873} = -58{,}500$ cal.

Proper combination of the values given in (*a*), (*b*) and (*c*) yields:

(*d*) Si (liquid) = Si (in Fe) ; $\Delta G^\circ_{1873} = -29{,}700$ cal.

This result represents the free energy of solution of silicon at unit activity on a scale in which the activity is equal to percentage at infinite dilution. To convert this to activity on a mole fraction scale in which the activity of pure liquid silicon is unity requires the application of eqn. (16) which gives:

$$(e)\quad -29{,}700 = 4{\cdot}575 \times 1873 \log \frac{a_{\text{Si}}\ (\text{dil. soln.})}{a_{\text{Si}}\ (\text{pure})}$$

from which the ratio of the activities of silicon on the two scales of measurement is 0·00034. The mole fraction of silicon in dilute solutions is 0·0199 times its weight-% hence the standard state corresponds to a mole fraction of 0·0199 and the activity referred to pure silicon is 0·00034, from which the activity coefficient is 0·017. This is the quantity which we have called γ° and whose logarithm is plotted at point D in Fig. 16 to complete the activity curve of silicon in iron.

The activity and activity coefficient in dilute solutions have been calculated from the curve of Fig. 16 and are shown in Fig. 25 on a weight-% basis. Here the activity coefficient is defined as $f_{\text{Si}} = a_{\text{Si}} / \%$ Si. Its value is unity at infinite dilution and is found to be a linear function of concentration up to about 14 %.

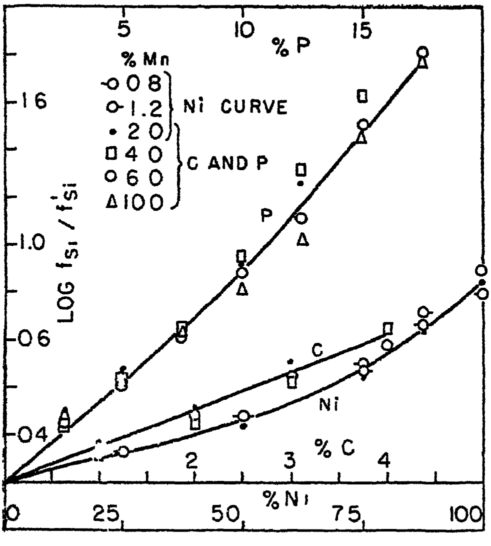

FIG. 26.—Effect of additions on the activity coefficient of silicon in liquid iron.

Activities in Three-component Solutions

Up to this point nothing has been said about activities in metallic solutions of three or more components. Useful generalisations regarding such systems are not plentiful and the amount of experimental data is meagre. We shall examine a number of ternary solutions in which iron is the major constituent and focus our attention upon the effect of one minor component upon the activity of a second.

Effect of Additions on the Activity of Silicon in Liquid Iron.—Körber [49] studied the influence of additions on the reactions between molten alloys consisting principally of iron and manganese with silicate slags saturated with solid silica. The principal reaction is:

$$SiO_2\ (\text{solid}) + 2Mn\ (\text{in Fe}) = Si\ (\text{in Fe}) + 2MnO\ (\text{in satd. slag}).$$

Equilibrium was studied at several manganese levels up to 10%. Previous work had shown that the activity of silicon was not affected by manganese within this range and Körber's results indicated further that the activity of manganese was essentially unaffected by the addition agents. The activity of manganese may be taken as equal to its weight-%, since it forms a nearly ideal solution in liquid iron. The activity of silica is fixed by the presence of solid SiO_2 and that of MnO in the slag is approximately constant. Therefore at any given concentration of manganese in the metal the activity of silicon is constant. Any variation in the percentage of silicon at equilibrium is due to the effect of the added element upon its activity coefficient. The activity coefficient of silicon, *f*, in each of Körber's melts has been computed. The value of *f* at any given silicon concentration in pure iron silicon alloys is designated *f'*. Körber's data are summarised in Fig. 26 in which the logarithm of *f*/*f'* is plotted against the weight-% of added element. From these curves and values of *f'* for silicon from Fig. 25 the activity of silicon may be computed for any ternary alloy within the composition range covered.

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[48] *Basic Open Hearth Steelmaking* (Amer. Inst. Min. Met. Eng., New York, 1944).

[49] Körber, *Stahl Eisen*, 1937, 57, 1349.

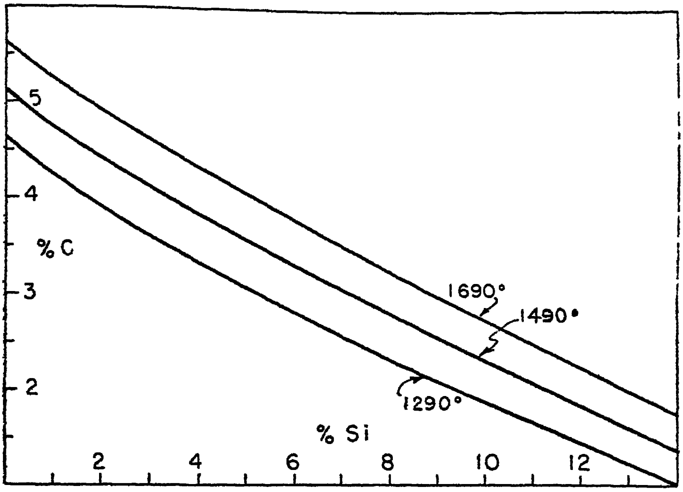

FIG. 27.—Solubility of graphite in molten iron-silicon alloys at several temperatures (Small and Wilson).

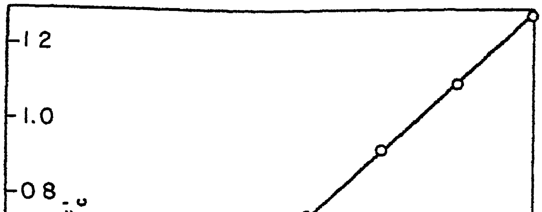

FIG. 28.—Effect of silicon on the activity coefficient of carbon in liquid iron.

Effect of Silicon on the Activity of Carbon in Liquid Iron.—Silicon decreases the solubility of graphite in liquid iron and therefore increases the activity coefficient of carbon. The solubility of graphite in iron-silicon alloys at three temperatures determined by Small and Wilson [50] is shown in Fig. 27. Since the activity of carbon is fixed

[50] Small and Wilson, *S. B. Thesis* (Mass. Inst. Tech., 1942).

by the presence of graphite, the decreased solubility is credited to an increase in activity coefficient of carbon in the presence of silicon. At 1490° the solubility in pure iron is 5·13 % C and the value of f_C from Table VII is 6·6. Hence, the activity of C in the entire series at this temperature is 33·8. At 2 % Si the solubility is only 4·40 % C and the value of f_C is therefore 33·8/4·40=7·68. At the same carbon content in pure Fe–C alloys the activity coefficient, designated here f'_C, is 4·7. The logarithm of the ratio f_C/f'_C is plotted against concentration of silicon in Fig. 28, in which it is seen that the relationship is linear. On the basis of the simple assumption that the same ratio is valid for unsaturated alloys, the activity of carbon may be had at any composition in the ternary liquid solution up to 14 % silicon.

The results of this calculation are shown in Fig 29 together with the activities of silicon in the same solutions. The data are for a temperature of 1490° and the activity of carbon, which is shown on a scale of unit activity for graphite, must be restricted to this temperature. The silicon activities being based upon infinite dilution will not vary greatly with temperature; the carbon activities may be referred to infinite dilution by multiplying by 33·8.

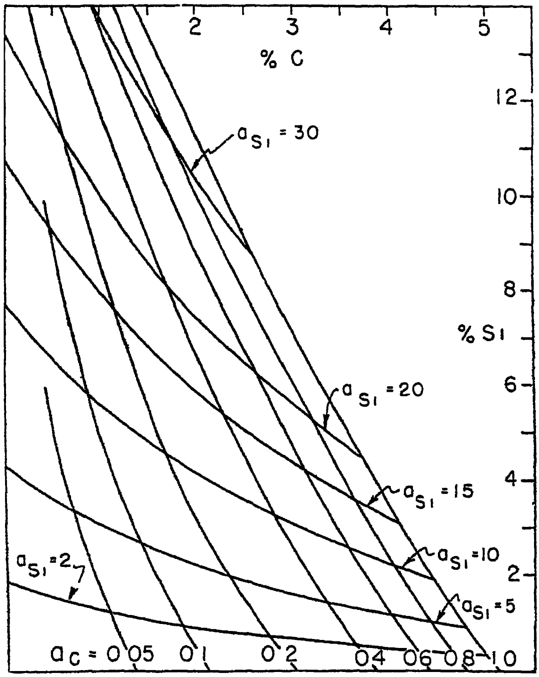

FIG. 29.—Activities of carbon and silicon in Fe-C-Si alloys.

Conclusion

Such a rambling discussion cannot well be summarised without tiresome repetition. Suffice it to say in summary that the concept of activity and the thermodynamic equations involving it have been reviewed. The well-known methods for determining activities have been illustrated by data on liquid metallic solutions. The concept of semi-regular solutions has been introduced and its usefulness for metals demonstrated. Several useful empirical methods of treatment of activity data have been employed.

It should be pointed out that this paper is in no sense a complete review of the literature on the subject. An extensive bibliography as well as a detailed discussion of the thermodynamics of solid and liquid metallic solutions by Wagner[51] is included in Masing's *Handbuch der Metallphysik*. Other very useful reviews and discussions are those of Sauerwald[52] and of Kubaschewski.[53] It has not been possible here to refer to all of the important papers in the field and many interesting researches such as those on very dilute amalgams have been omitted from consideration. No attempt has been made to treat the thermodynamics of solid solutions in which ordering plays so prominent a part. Nor has adequate consideration been given to the effects of differences in internal pressure, atomic volume, interatomic potentials and the like, which may in the future provide a useful approach to the thermodynamics of alloys.

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[51] Wagner, Vol. I, Part III, in Masing's *Handbuch der Metallphysik* (Leipzig, 1940).
[52] Sauerwald, *Z. Metallkunde*, 1943, 35, 1905.
[53] Kubaschewski, *Z. Elektrochem.*, 1942, **48**, 559, 646.

It is hoped that this paper may serve at least as an introduction to the literature on metallic solutions and as a stimulus to the wider use of the activity concept in metallurgical problems.

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THE ACTIVITY OF SULPHUR IN LIQUID IRON : THE INFLUENCE OF CARBON

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The chief factor which determines the sulphur content of a finished steel is well known to be the ratio in which the sulphur is partitioned between the molten metal and the overlying slag with which it is in contact during the refining process. It is clearly desirable to have a detailed knowledge of this partition, with a view ultimately to substituting scientific control for the empirical methods of traditional practice. The need for improved measures for controlling sulphur is indicated by the demand for lower sulphur contents in special steels, the need for fuel economy and consequently minimum slag volume, and the simultaneous increase in the sulphur content of some of the raw materials which must now often be used.

The qualitative factors which influence desulphurisation have frequently been discussed,[1] but little accurate quantitative information is available. Essentially, the problem can be resolved into a study of the chemical potential (or thermodynamic activity) of sulphur in the metal and slag (and also in the furnace gases, since sulphur pick-up may occur during melting down of scrap iron). The present paper is concerned with the thermodynamic treatment of experimental results on the interaction of sulphur with iron.

The Activity of Sulphur in Pure Liquid Iron.

The partial pressure (p_{S_2}) of sulphur over its solution in liquid iron is too small to be measured directly, but it has been determined indirectly by several authors by using the reaction

$$H_2(g) + \tfrac{1}{2}S_2(g) = H_2S(g)$$

to produce the necessary sulphur. The equilibrium constant of this reaction is known at high temperatures from spectroscopic and other data.[2]

The reaction between H_2S and liquid Fe is formally similar to that previously studied at lower temperatures by several authors for the solid state, the equation for which is

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[1] (*a*) e.g., *Basic Open Hearth Steelmaking* (Physical Chemistry of Steelmaking Committee, 1944). (*b*) Carter, This Discussion.

[2] Kelley, *U.S. Bur. Mines, Bull.*, 1937, No. 406.

$$\mathrm{FeS\ (solid)} + \mathrm{H_2} = \mathrm{Fe\ (solid)} + \mathrm{H_2S}.$$

When both Fe and FeS are crystalline solids their activities (a_{Fe} and a_{FeS}) are constant and are conventionally taken as unity so that the equilibrium constant for this reaction is given by

$$K = \frac{a_{\mathrm{H_2S}}}{a_{\mathrm{H_2}}} = \frac{p_{\mathrm{H_2S}}}{p_{\mathrm{H_2}}}.$$

At temperatures above the melting point of iron a single liquid is present in place of the two crystalline phases, i.e., Fe + FeS, so that the $p_{\mathrm{H_2S}}/p_{\mathrm{H_2}}$ ratio is shifted. The iron-sulphur system in the molten state probably consists of $\mathrm{Fe^{++}}$ and $\mathrm{S^{--}}$ ions and their ion complexes together with electrons and thus ideally the reaction should be written

$$\mathrm{Fe^{++}} + \mathrm{S^{--}} + \mathrm{H_2} = (\mathrm{Fe^{++}} + 2e)_{\mathrm{metal}} + \mathrm{H_2S}.$$

At high sulphide concentrations there are some difficulties in formulating the equilibrium constant according to this equation, and from a formal and thermodynamic viewpoint, the constitution of the melt does not play an essential part in the treatment.

The equation may hence be formally written:
Iron sulphide (in solution in Fe) + $\mathrm{H_2}$ = Fe (in solution) + $\mathrm{H_2S}$, for which

$$K = \frac{a_{\mathrm{Fe}}\, p_{\mathrm{H_2S}}}{a'\, p_{\mathrm{H_2}}}$$

where a' denotes the activity of the " sulphide " component in the melt and which may be considered as the resultant activity of iron and sulphide ions. Following the usual convention, the standard state for iron can be pure liquid iron at the same temperature and for the " sulphide " component a (1 : 1) iron-sulphur liquid mixture at the same temperature. With these conventions, the last constant K remains comparable with that previously used for the reaction involving solids.

The implicit assumption is made in the equilibrium studies that the presence of hydrogen in the iron does not influence the activity of sulphur appreciably: this seems justifiable as the solubility is low (0·003 %) and the hydrogen atom is too small to cause large disturbance of the structure of the liquid metal. Hence, by combining the above equilibria, the partial pressure of sulphur over the melts is obtained.

Chipman and Ta Li[3] made measurements of the above equilibrium between 1535 and 1600° C. and for sulphur contents up to 1·27 %. Their results indicated that at equilibrium the amount of sulphur in the iron was directly proportional (within experimental error) to $p_{\mathrm{H_2S}}/p_{\mathrm{H_2}}$ in the gas phase up to at least 1·2 %. When this result is taken in conjunction with the above equilibria it follows that the sulphur content of the metal is proportional to the *square root* of the vapour pressure of sulphur (considered as $\mathrm{S_2}$, its stable form at these temperatures). Thus, Sievert's law holds for sulphur in iron as it does for hydrogen, oxygen, and nitrogen. Since Henry's law is usually the rule applicable at extreme dilution, cases of Sievert's law are generally explained by postulating that the diatomic gas in its molecular form ($\mathrm{S_2}$) does not dissolve as such in the metal, but that it dissociates and is in equilibrium with a certain partial pressure of mon-atomic material (S) which is soluble and obeys Henry's law.

However, it is apparent from the large departures from ideality shown by the freezing points of mixtures of FeS and Fe[4][5] that Henry's law can hold only for very dilute solutions. Although the liquids are completely miscible, the liquidus shows a point of inflexion at about 15 % sulphur and, according to Darken and Larsen,[6] the positive deviations from ideality are so great that the system cannot be far from immiscibility. If this view is correct, the ratio p_{H_2S}/p_{H_2} cannot remain proportional to the sulphide content for more than a very short range for the following reasons. The solute in a non-ideal solution approximates to Henry's law in very dilute solutions, but the activity coefficient must eventually fall, approaching unity as the composition approaches the pure component, for which Raoult's law is the applicable rule. The ratio p_{H_2S}/p_{H_2} can be regarded as a measure of a' for dilute solutions since

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[3] Chipman and Ta Li, *Trans. Amer. Soc. Met.*, 1937, **25**, 435.

$$\frac{p_{H_2S}}{p_{H_2}} = \frac{K\,a'}{a_{Fe}}$$

and both K and a_{Fe} are constant under these conditions. Consequently, if the sulphide shows large positive deviations from ideality, the value of p_{H_2S}/p_{H_2} may be expected to increase less rapidly at higher sulphur contents than predicted by Henry's law.

This is found to be the case. White and Skelly[7] have recently studied the equilibrium between Fe and H_2S by a slightly modified technique. Their results are in good agreement with those of Chipman and Ta Li, but extend up to 3·5 % sulphur. White and Skelly did less than justice to their own work by presenting the results as a table of values of K, which they implied should remain constant, although no account was taken of the variation of activity coefficient with concentration. If their data (recalculated) are plotted as p_{H_2S}/p_{H_2} against the percentage of sulphur in the metal, it is apparent that they lie on a pronounced curve, the effective activity coefficient decreasing with increasing sulphur content (Fig. 1).

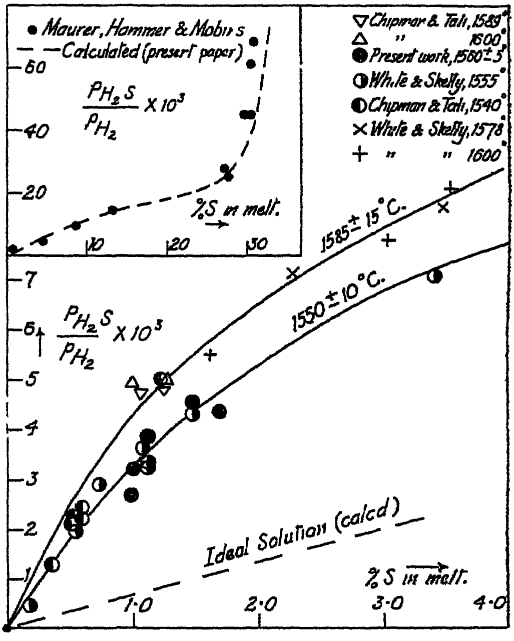

FIG 1.—Summary of results of various authors for the equilibrium between H_2–H_2S mixtures and liquid iron.

The only other reliable measurements of this equilibrium for the *liquid* state are those of Maurer, Hammer and Möbius[8] which are chiefly concerned with high sulphur contents approaching the composition $\frac{\text{Fe}}{\text{S}} = 1$. These workers obtained a number of results for melts with less than 2 % sulphur, but the values are too scattered to give any information on the present subject. Their high-sulphur results for 1475° C. are shown in the inset to Fig. 1 and the effect of decreasing activity coefficient is marked between 0 and 15 % S. The sulphur activity rises, however, very steeply beyond 25 % S.

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[4] Miyazaki, *Sci. Rep. Tohoku Imp. Univ.*, 1928, **17**, 877.
[5] Loebe and Becker, *Z. anorg. Chem.*, 1912, **77**, 301.
[6] Darken and Larsen, *Trans. Amer. Inst. Min. Met. Eng.*, 1942, **150**, 87.
[7] White and Skelly, *J. Iron Steel Inst.*, 1947, **155**, 201.
[8] Maurer, Hammer and Mobius, *Arch. Eisenhuttenw.*, 1942, **16**, 159.

The general form of this graph may be explained as the result of a decreasing activity coefficient of sulphide together with the normal influence of mass action, the ratio p_{H_2S}/p_{H_2} depending on both a_{Fe} and a'. For a wide concentration range a rising sulphur activity is necessarily accompanied by a falling iron activity, and both of these factors influence the partial pressure of sulphur vapour over the solution. An approximate interpretation of the form of the graph can be made in the following way.

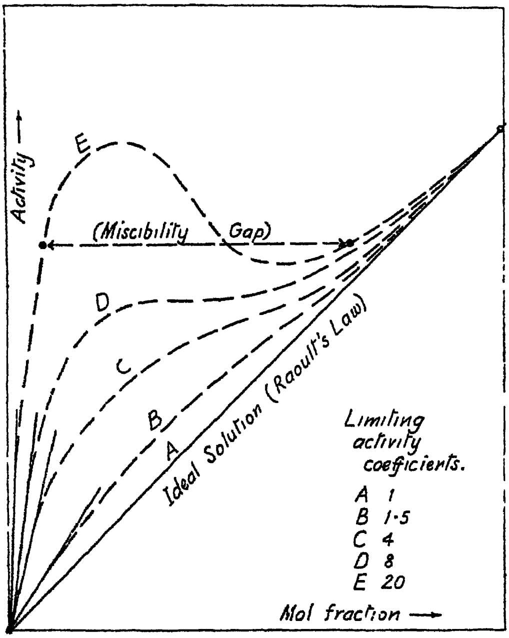

Fig. 2.—Typical positive deviations from Raoult's law.

Darken and Larsen made a rough estimate of the "activity coefficient" of sulphide in dilute solution in iron. They arrived at a value of 4·5 by three independent arguments based on (*a*) the data of Bardenheuer and Geller [9] for the partition of sulphur between iron and FeO — FeS slags, (*b*) the work of Körber [10] on the partition of sulphur between iron and FeS — MnS slags, and (*c*) the discrepancy noted by Chipman and Ta Li between their own results for sulphur in liquid iron and the value which they extrapolated from the measurements of Britzke and Kapustinsky [11] for solid FeS. The excellent agreement found between these three calculations was admittedly fortuitous in view of the assumptions involved and the limitations of the original experiments, but the true value of the activity coefficient in dilute solution in iron may probably be in the region of 4.

The *general form* of the relation between partial pressure and composition in a two-component system showing positive deviations is well known [12] but the exact course of the activity-mol fraction line may vary from one system to another, and although expressions have been proposed to represent such curves [13] they are not universally applicable. Thus the value of the activity coefficient of a solute at infinite dilution alone is not sufficient to enable the rest of the curve to be predicted accurately. However, it can be expected [12] to take a form similar to one of the lines shown diagrammatically in Fig. 2, which are for a series of systems showing increasing positive deviations leading up to immiscibility. From the above-mentioned calculation of Darken and Larsen,[6] it follows that the activity curve of sulphide in iron must depend on composition in a way similar to line C, i.e., the initial value of the activity coefficient being here about 4·5. As this type of behaviour is known to occur in metal-metal systems, e.g., amalgams,[14] there seems no reason why the deviations from ideality in the present system should not be of the same type. When one component in a two-component system shows positive deviations, the other usually behaves in a very similar fashion* ; a' and a_{Fe} may, therefore, be expected to change in roughly the same way with mol fraction. On this basis it is possible to calculate approximately the general shape of the p_{H_2S}/p_{H_2} — % S curve using the values of activities on curve C at the same mol fractions.

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[9] Bardenheuer and Geller, *Mitt. Kaiser Wilhelm Inst. Eisenforsch.*, 1934, **16**, 77.

[10] Körber, *Stahl Eisen*, 1936, **56**, 433.

[11] Britzke and Kapustinsky, *Z. anorg. Chem.*, 1930, **194**, 323.

[12] cf., Hildebrand, *Solubility of Non-electrolytes*, 2nd Edn. (1936).

[13] Porter, *Trans. Faraday Soc.*, 1921, **16**, 336.

The values calculated in this way are shown as the broken line in Fig. 1 (inset), the value of K being taken as 0·02 for an equimolar mixture of Fe and FeS.[8] It is seen that the general form of the results of Maurer, Hammer and Möbius is satisfactorily accounted for by this treatment. More precise analysis cannot be made until more accurate measurements become available.

The Influence of Carbon.

In practice desulphurisation of iron is carried out with metal containing various other elements, notably carbon, manganese and silicon in addition to iron. It is, therefore, necessary to know how these other components influence the activity of the sulphur. For example, it is recognised that " sulphur is best eliminated when the oxygen content of the bath and slag is low, so that control to remove sulphur should be started at an early stage when the carbon is high." [15]

The general effect of a third component which is immiscible with either iron *or* iron sulphide would be to enhance still further the tendency to immiscibility by increasing the positive deviations from Raoult's law and thus forcing the system to approach, for example, curve D and eventually E in Fig. 2. Whereas the Fe–FeS and Fe–Fe_3C pairs are completely miscible, according to Hanemann and Schildkötter [16] and to Vogel and Ritzau [17] respectively, there is a miscibility gap in the Fe_3C–FeS system. Consequently, the presence of carbon in the Fe–S system may be expected to increase a'.

Evidence in support of this conclusion has been advanced by Darken and Larsen based on unpublished measurements of Gurry [18] in which the saturation solubility of iron sulphide in Fe saturated with carbon was found to be 1·5 % S at 1500° c. More recently a detailed investigation of the conjugate solutions in the Fe–FeS system saturated with graphite has been carried out by Norro and Lundquist [19] who find that at 1550° c. the metal layer contains about 3 % sulphur and rather more than 4·5 % carbon,† while the sulphide layer contains about 26·5 % sulphur and 0·5 % carbon. Darken and Larsen considered the sulphide layer to be practically equivalent to pure FeS, whereas Norro and Lundquist formulated it as 75·5 % FeS, 7·5 % Fe_3C and 17·0 % Fe. The molecular constitution of liquids containing Fe, S, and C is as yet uncertain, apart from the fact that it is extremely improbable that it consists of definite compounds, so that it is not possible to calculate the mol fraction of " FeS " unambiguously, but an equivalent value of 0·7 mol. is probably a more accurate estimate than 1 mol.

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[14] Eastman and Hildebrand, *J. Amer. Chem. Soc.*, 1914, **36**, 2020.
[15] See ref. 1 (*a*), p. 186.
[16] Hanemann and Schildkötter, *Arch. Eisenhuttenw.*, 1929, **3**, 427.
[17] Vogel and Ritzau, *Arch. Eisenhuttenw.*, 1931, **4** 549.
[18] Darken and Larsen, *loc. cit.*, and Darken, private communication.
[19] Norro and Lundquist, *Jernkontorets Ann.*, 1946, **130** (3), 118.

* The two are, of course, related by the Gibbs-Duhem equation.
† Estimated, not expt., value.

It can be seen from Fig. 2 that the activity coefficient of a component in a mixture showing immiscibility remains practically constant up to the first conjugate solution if the gap is wide. Therefore, since 3 % sulphur corresponds to a mol fraction of sulphide of 0·054, the activity coefficient must be given by 0·7/0·054 = 13. This is to be compared with the activity coefficient in pure iron which is about 4·5 (see above). Hence, the presence of about 5 % carbon has increased the activity of sulphur about *three times*.

Another rough estimate of the effect of carbon can be made from some results of Meyer and Schulte [20] on the two-phase equilibria in the Fe–FeS–MnS system. They carried out some experiments at 1600° c. with added carbon (in addition to more numerous measurements in the absence of carbon). The mean of eight concordant results with carbon shows that a metal layer containing 6·24 % Mn, 2·55 % C and 0·15 % S is in equilibrium with a slag containing 4·0 % Fe, 54 % Mn and 30·4 % S. A typical example from the carbon-free series which is fairly closely comparable is one (No. 77 in Table 2 of the above quoted work) in which the slag was 4·1 % Fe, 54·3 % Mn and 29·4 % S. This was in equilibrium with metal containing 4·15 % Mn and 0·513 % S. The slags were therefore almost identical whereas 0·15 % S was present in the metal containing carbon to 0·513 % in the absence of carbon. Thus the activity of the sulphur has been increased by a factor of 3·4 times.

By comparison with other of the carbon-free melts analysed by Meyer and Schulte (in which, however, the slags were slightly different) a factor of about *two* is indicated. Making allowance for the fact that the carbon content of the melts referred to above was found to be 2·55 %, it appears that these results are in reasonable agreement with the estimate of *three times* already arrived at for the influence of saturation with graphite on the sulphur activity. However, all these estimates must be treated with reserve, since the measurements and assumptions involved are open to criticism.

In view of the importance to technology of obtaining more reliable information on this problem by *direct* means, it was decided to carry out measurements of the sulphur uptake of iron at equilibrium with H_2S–H_2 gas mixtures in the presence of graphite. It would be possible, in principle, to use the equilibrium, $C + S_2 = CS_2$, as a means of procuring a known sulphur activity for this determination, but such a method is not practicable since the requisite partial pressure of CS_2 (for example, in an inert carrier gas) would be so low that enormous volumes of gas would be needed to transport the quantities of sulphur involved.

The H_2S–H_2 mixture can be used in this determination in the same way as for pure iron because the loss of sulphur by formation of CS_2 and of hydrogen as CH_4 occur to relatively small extents and corrections can be applied if necessary to obtain the true partial pressure of sulphur vapour in the C–H_2S–H_2 equilibrium mixture. The partial pressures (in atm.) in this mixture at 1550° c. would be roughly $H_2 = 1$, $H_2S = 4 \times 10^{-3}$, $CS_2 = 9 \times 10^{-5}$, $CH_4 = 5 \times 10^{-4}$ and $S_2 = 1{\cdot}6 \times 10^{-5}$. If allowance is made for the fact that the [H_2S] is reduced by the formation of CS_2 (using extrapolated equation for the free energies of these compounds taken from

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[20] Meyer and Schulte, *Arch. Eisenhuttenw.*, 1934, **8**, 187.

Kelley [21]), the final pressure of S_2 is reduced by about 9 % below the above value. Consequently, in comparing activities of FeS in Fe with and without carbon this allowance should strictly be made. Results of the present work will be reported directly in the H_2S/H_2 ratios employed.

Experimental

The method used was similar in principle to that of previous workers, i.e., a known H_2S–H_2 mixture was passed over liquid iron until equilibrium was reached, when the metal was quenched and analysed for sulphur. Single droplets of iron were employed [22] as they facilitated attainment of equilibrium and the eventual analysis (segregation difficulties being obviated by analysing the whole bead). The danger of contamination of the sample by volatile silicon compounds (SiO or SiS) derived from the furnace tube was first clearly noted in the work of White and Skelly.[22] The samples of these workers contained as much as 2 % Si derived from the source. Preliminary experiments confirmed White and Skelly's observations in this respect and also brought to light the very large error which may be incurred by assuming that, if a known H_2S–H_2 mixture is passed slowly into a wide furnace tube, the gas at the centre of the tube has the same composition as the gas entering. It was, in fact, much lower in sulphur content, partly due to thermal diffusion,[23] but more to reaction with the mullite furnace tube which was generally rendered useless after about a week's use. Pure recrystallised alumina was also found to take up sulphur to a large extent, although it was not badly damaged thereby. The fact that large amounts of aluminium could later be dissolved out of it by cold dilute HCl suggests that some aluminium sulphide is formed.

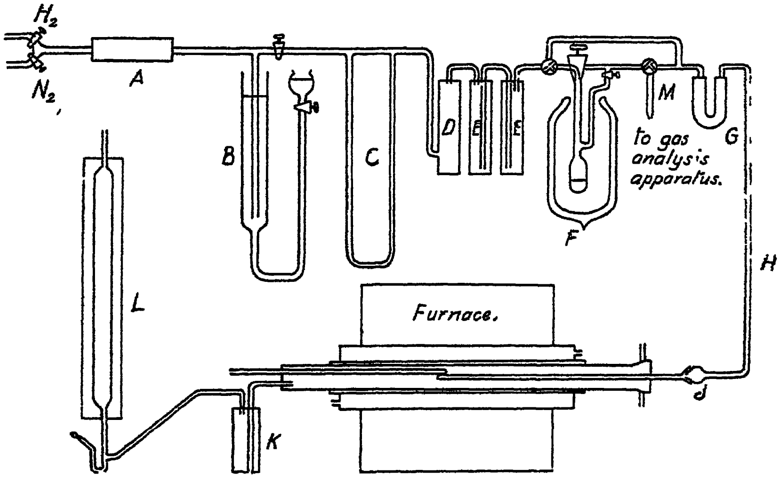

FIG. 3.—*General arrangement of experiment.* A, palladised asbestos. B, manostat. C, capillary flowmeter. D, $CaCl_2$. E, H_2SO_4. F, H_2S "saturator." G, anhydrone. H, flexible polythene tubing. J, ground-glass joint. K, lead acetate solution. L, soap-bubble flowmeter. M, 3-way stopcock for sampling gas.

The final method developed was successful in eliminating both siliceous contamination and errors due to thermal diffusion. It was convenient and rapid and is believed to be an improvement on previous techniques. The general arrangement of apparatus is shown diagrammatically in Fig. 3, which is self-explanatory except for the following points.

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[21] Kelley, *U.S. Bur. Mines. Bull.*, 1937, **406**, 18, 30.
[22] White and Skelly, *loc. cit.*
[23] Emmett and Shultze, *J. Amer. Chem. Soc.*, 1933, **55**, 1390 ; see also Chipman and Dastur, This Discussion.

H_2S–H_2 Mixtures.—A constant, adjustable rate of flow of H_2 (controlled by B and C) was passed through the vessel F which contained liquid H_2S [24] in a Dewar flask in solid CO_2. Diffusion of H_2S into the H_2 stream occurred to an extent controlled by the dimensions of the apparatus and was constant for a constant rate of gas flow. The proportion of H_2S in the resulting gas could be altered by changing the H_2 rate, or by restricting the lower part of the tube by inserting glass capillaries into the apparatus through the 3-way tap, or by altering the pressure (and hence the temperature) over the solid CO_2. This method of obtaining the gas mixtures had advantages in some circumstances over the method of batch mixtures prepared in steel cylinders used by previous workers, e g., for very long runs or for a series of very short runs where different concentrations were needed.

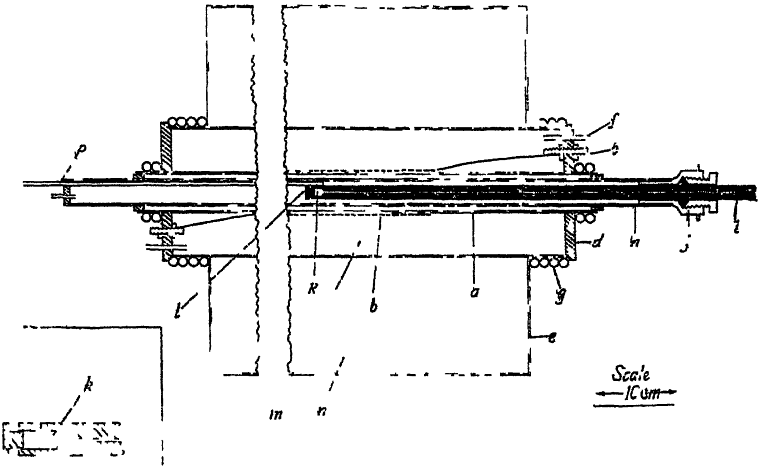

Fig. 4.—*Details of furnace.* *a*, mullite furnace tube. *b*, molybdenum strip winding. *c*, terminal. *d*, asbestos-cement end-plate. *e*, iron furnace case. *f*, outlet for hydrogen. *g*, water cooling. *h*, inner mullite tube. *i*, pure carbon capillary tube. *j*, water-cooled brass stopper with asbestos gasket. *k*, reaction chamber, *l*, graphite stopper closing reaction chamber. *m*, alumina powder. *n*, asbestos insulation. *p*, thermocouple sheath.

The Molybdenum Furnace (Fig. 4) was made in the laboratory. In the early stages the heater unit had frequently to be replaced owing to breakdown of the mullite furnace tube as a result of reaction with the gases, but later an inner mullite combustion tube was inserted. This had a rubber bung at one end (protected from heat by a refractory baffle and carrying the alumina or mullite, impermeable, thermocouple sheath), and a special double-walled water-cooled brass stopper at the other. This was fitted with an asbestos-packed gas-tight gland, through which a graphite or alumina tube could be rapidly inserted or withdrawn without altering the temperature of the furnace. Temperature was measured to ± 2° with a Pt/Pt–Rh thermocouple and potentiometer sensitive to 0·02 mv., the couple being normally kept withdrawn inside the sheath out of the hottest zone to prevent deterioration. It was pushed to the end of the sheath when a reading was to be taken, and left until the reading was constant. The thermocouple sheaths rarely withstood the H_2–H_2S mixture for more than a few days. Consequently, the thermocouple was later replaced by a disappearing-filament optical pyrometer which was sighted on the end of the carbon reaction chamber. In comparative tests the thermocouple and pyrometer were found to be in excellent agreement, the mean of a series of concordant readings on the two instruments differing by $<3^{\circ}$ at 1595° c. After 12 hr. heating the furnace was generally constant to within $\pm 5^{\circ}$ for long periods.

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[24] Habermann, *Chem. Zentr.*, 1890 (4), 282; *Inorganic Syntheses* (1939), Vol. 1.

The Reaction Chamber (inset Fig 4) was a small cavity drilled in the graphite capillary tube, with a graphite stopper and a vent hole. This device was an important feature of the design, as it ensured (*a*) that thermal diffusion was eliminated, since the whole of the chamber was at uniform temperature and the gas streamed rapidly into, and out of, the chamber—too fast for back diffusion to occur.* Further the incoming gas was heated by passing through several inches of hot capillary before entering the chamber ; (*b*) no contamination of the sample with silica from the mullite tube and simultaneous changes in gas composition was possible. Taken together, these points guaranteed that the gas mixture in contact with the sample was identical with that entering the inlet tube. Another important feature of this design was that rapid quenching was possible, and a series of samples could be treated consecutively in a short time.

Iron used in various runs was either pure Swedish iron drillings, or carbonyl iron powder,[25] or electrolytic iron granules.[26] All of these contained only traces of impurities and no differences could be detected between results with the different materials. When it was required to approach equilibrium from the other side, a mixture of ferrous sulphide powder (previously made by heating together carbonyl iron powder and flowers of sulphur in stoichiometric proportions), and carbonyl iron was used. The 0·2 to 0·7 g of starting materials was placed as a loose heap inside the reaction chamber where it fused into a single bead.

Procedure.—With the furnace at the required temperature, the carbon tube carrying a fresh sample was inserted a short way into the furnace with a stream of nitrogen passing through it. The nitrogen was followed by H_2S–H_2 mixture for a few minutes and the graphite tube was then pushed further in until the sample was at the centre of the heated zone (as shown by a mark on the carbon tube). Either during, or immediately after, the reaction period a sample of the gas mixture was by-passed at M for analysis by absorption in alkaline hypochlorite solution, the manostat B being adjusted, if necessary, to maintain exactly constant flow through the " saturator " (as indicated by C). The absolute rate of flow through the furnace could be measured by the soap-bubble flowmeter at the exit end.

At the end of a run the graphite tube was withdrawn steadily with the gas mixture running until the reaction chamber was inside the water-cooled stopper. Quenching was very rapid owing to conduction through the graphite and in about one minute the tube could be taken out completely, the gas mixture being first swept out of the furnace by nitrogen to prevent explosion. The resulting iron bead was extracted easily by removing the graphite stopper, and weighed for analysis.

Analysis.—Attempts to analyse the gas and the iron samples by the standard volumetric method based on oxidation of an alkali or cadmium sulphide with iodine proved unsatisfactory.† An improved method was developed after some time, details of which will be published elsewhere. It is based on oxidation of alkali sulphide by means of alkaline hypochlorite. It has many advantages over the iodine method and is believed to give reliable and absolute results correct to ± 1 % of the sulphur content, provided a number of important precautions are strictly observed.

[25] Kindly provided by The Mond Nickel Co. Ltd.

[26] Kindly provided by Messrs. George Cohen Sons & Co. Ltd.

[27] Kolthoff and Sandell, *Textbook of Quantitative Inorganic Analysis* (1943), p. 720.

* Approximate estimates of the extent of thermal diffusion, carried out by Mr. E. Whalley, indicated that the error in concentration in this apparatus with a flow of 1 cc./sec. through a 2-mm. tube should certainly be less than 0·3 %.

† It is recognised that none of the many methods of determining sulphur in steel is stoichiometrically *absolute*, i.e., they are all semi-empirical and yield correct values only if carried out in precisely the standard fashion. Larger or smaller samples or sulphur contents may lead to erroneous results.[27]

For the gas analysis, a known volume (measured, after absorption of H_2S, in a water-jacketed calibrated flask or by means of a soap-bubble flowmeter) was passed through a conical flask containing a known volume of standard alkaline hypochlorite, which was afterwards boiled, cooled and titrated. For the iron beads, the H_2S evolved by dissolution in acid (with rigid exclusion of air) was similarly absorbed and determined volumetrically. Subsidiary tests proved that all the sulphur was evolved as H_2S from the samples encountered in this work, whether with or without carbon.

It was noticeable that some samples of high sulphur content containing large amounts of graphite, were very slow to dissolve whereas others of small sulphur content dissolved rapidly and left little or no graphite. This is due to the well-known effect of sulphur in inhibiting the transformation of cementite (Fe_3C) into graphite, as in white cast iron. No notable differences were found between sulphur contents of the graphitised and non-graphitised specimens.

No noticeable amount of silicon was found in the samples. Those prepared in the absence of carbon gave absolutely clear solutions in acid

Attainment of Equilibrium.—Information as to the rate of attainment of equilibrium between Fe and H_2S in the literature is scanty, but the general impression is that it is very slow. Thus Chipman and Ta Li's tests indicated that at least 10 hr. would be needed to attain equilibrium with a 50 g. sample starting as pure Fe; however, absorption of sulphur by the magnesia crucible invalidated this test. White and Skelly allowed about 6½ hr. for attainment of equilibrium with 1 g. samples, without apparently investigating the effect of time. The reverse reaction was thought to be slow and no attempt was made to quench the melt. No difference was found when the samples were cooled in the gas mixture or in pure hydrogen. However, these observations prove nothing about attainment of equilibrium, as (*a*) the temperature coefficient of the equilibrium constant is relatively small, and (*b*) as mentioned above, alumina picks up very large quantities of sulphur during the experiment and this sulphur is evolved as H_2S for many hours after the gas mixture is replaced by pure hydrogen.

The present work leads to a different conclusion: namely, that the reaction between iron and the H_2S–H_2 mixtures is rapid at 1560° c. and equilibrium is attained almost as soon as the requisite quantity of sulphur can be transported by the gas mixture. This conclusion is based on the following tests. (*a*) ½ g. samples of pure iron were heated for ¼, ½, 1, and 2 hr. Considerable sulphur pick-up occurred even in ¼ hr. and the sulphur content was constant after 1 hr. (*b*) In tests in which the equilibrium was approached from both sides, samples starting with 2 % S finished at 0·3 % S after 1 hr. and were concordant within experimental error with others which started as pure Fe and had also received 1 hr. treatment. It is believed that the above considerations prove that equilibrium was attained in the present experiments. It may be pointed out that the chief factor governing this rapid attainment of equilibrium was the small mass and large available surface of the samples.

Results

It is possible to report here preliminary results obtained by the above procedure.*

A few measurements of the equilibrium were first made at 1560±5° c. in the absence of carbon, using an alumina reaction tube packed with alumina capillaries to ensure a fast linear rate of gas flow. The results are shown in Fig. 1 together with those of previous workers, with which they are seen to agree well. This tends to confirm both the existing data and the validity of the experimental methods used here.

It is noticeable that although the present samples contained no appreciable quantity of silicon while those of White and Skelly contained *ca.* 2 % Si, there is no significant difference between the results of these and the present authors. Silicon, therefore, seems to have little influence on the activity of sulphur in iron.

Approximate preliminary results for iron saturated with carbon are shown in

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* The work is continuing and it is intended to publish further details elsewhere.

Fig. 5 It can be seen that the activity of sulphur (as measured by the p_{H_2S}/p_{H_2} ratio) has been approximately *doubled* by the presence of carbon.

This *direct* evidence therefore supports the lowest of the indirect estimates discussed above. The fact that desulphurisation of iron can be most effectively carried out while the carbon content is high, i.e., at the pig-iron stage, is probably to be ascribed chiefly to a low oxygen activity in the slag, but the present results show that the influence of carbon on the sulphur itself is a contributory factor favouring desulphurisation

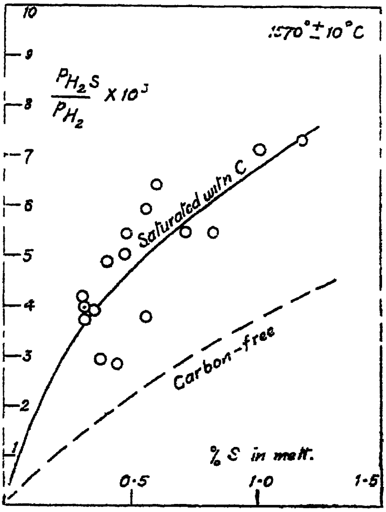

FIG. 5.—Preliminary results for the activity of sulphur over melts saturated with carbon at 1570° ± 10° c.

Discussion

In seeking a theoretical interpretation of the influence of carbon on the sulphur activity, a mechanism is required by which carbon *displaces* sulphur. *On the classical thermodynamic theory* this would be found in the reduced activity of free iron in these melts, which would be ascribed to formation of Fe_3C. For example, Darken[28] has shown that the freezing point of Fe–C solutions could be satisfactorily accounted for by supposing that the melt saturated with carbon at 1600° c. contains the following mol fractions of constituents:

$$Fe_3C = 0\cdot37, \quad Fe = 0\cdot56, \quad C = 0\cdot07.$$

It is undoubtedly true that the activity of iron is considerably reduced by carbon, as evidenced by the freezing point depression. It is possible to make an estimate of the extent without postulating the existence of the definite compound Fe_3C, e.g., by supposing that both liquid and solid solutions of Fe–C are ideal, so that the well-known formula

$$\log_{10}\frac{N(\text{soln})}{N(\text{solid})} = \frac{\Delta H}{2\cdot3R}\left(\frac{1}{T_0} - \frac{1}{T}\right)$$

can be applied. This argument leads to a value of 0·6 for the activity of iron in a melt with 5 % carbon which is about the same as deduced in another way above. Further, this figure would account for the greater part of the influence of carbon on the activity of sulphur in the melt, since reducing a_{Fe} by a factor of 0·6 would be equivalent to increasing the activity of sulphur in equilibrium by a factor of $1/0\cdot6 = 1\cdot7$, without allowing for any direct effect of carbon on the sulphur component itself.

It seems highly improbable, however, that compounds such as FeS and Fe_3C exist in solution as molecular entities corresponding to these formulæ. Compounds with approximately stoichoimetric proportions separate out on cooling but this is mainly because a regular crystal lattice with equal numbers of positive and negative charges is a stable configuration. Even in this crystal, however, there is no suggestion of FeS or Fe_3C molecules. Thus, in crystalline ferrous sulphide each sulphide ion is surrounded by *six* ferrous ions, the Fe–S distance being 2·45 A.[29] In cementite, each carbon is surrounded by 6 Fe ions at the apices of a distorted trigonal prism, the Fe–C distance ranging from 1·89 to 2·15 A. It seems to follow from recent electrochemical work that melts from pure FeS and Fe_3C are disordered versions of their respective crystal lattices. Liquid " FeS " is probably at least partially an ionic melt.[30] Mixtures of the melts will, therefore, probably be some resultant of the two liquid structures which, however, are obviously not mutually compatible, the carbon and sulphur competing for iron atoms with which to form their preferred co-ordination shell. A mixture of 5 % carbon in iron already contains only four iron atoms to every carbon. It is clear that the sulphur has a much reduced chance of forming its most stable structure with respect to iron neighbours. Consequently on the average the sulphur ions are less strongly held, i.e., their activity is increased.

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[28] Darken, *Trans. Amer. Inst. Min. Met. Eng.*, 1940, **140**, 204.

[29] Wells, *Structural Inorganic Chemistry* (1945).

This model would also suggest that there should be a reciprocal effect of sulphur on carbon,* the activity of which should be increased to an extent dependent on the relative tendency of the carbon and sulphur to co-ordinate to iron.

The authors' thanks are due to Dr. F. C. Tompkins and Dr. F. D. Richardson for valuable discussions, and to the British Iron and Steel Research Association for financial support of this work, including a B.I.S.R.A. bursary to one of us (A.L.).

Summary

Previous experimental work on the equilibrium between sulphur and iron has been reviewed. It has been shown that solutions of sulphur in iron, of compositions between pure iron on the one hand and a 1 : 1 iron-sulphur melt on the other, can be treated thermodynamically in chemical equilibria as binary mixtures of the two extremes and that these mixtures exhibit normal positive deviations from Raoult's law.

Indirect estimates of the influence of carbon on the activity of sulphur in iron are reviewed. Direct measurements have been made of the iron-sulphur equilibrium for melts saturated with graphite. Preliminary results show that saturation of the melt with the carbon approximately *doubles* the sulphur activity at 1560° c.

The mechanism of this increase of activity is discussed in terms of the probable structure of the melts.

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[30] Samarin, Tempkin and Schwarzmann, *Acta Physicochim.*, 1945, **20**, 421 ; Tempkin, *Acta Physicochim.*, p. 411 ; Bockris, Kitchener, Ignatowicz and Tomlinson, This Discussion.

* Possible evidence of this is the apparently lower solubility of carbon in melts containing sulphur ; Norro and Lundquist[19] found 4·2-4·3 % instead of the normal value of > 5 %. The effect has now been confirmed and is being investigated.

THERMODYNAMICS OF LEAD-ZINC ALLOYS

By John Lumsden

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1. Thermodynamic Equations

In this paper are given six free-energy equations from which can be derived the complete phase diagram and other thermodynamic properties of the lead-zinc system. Of these, four represent the free energy of fusion and of vaporisation of the components. A fifth equation represents the free energy of formation of liquid alloys. Finally, one equation is needed for solid solutions of zinc in lead ; the other solid phase is substantially pure zinc, the solubility of lead in which appears to be immeasurably small by any tests hitherto tried.

Of the vapour pressure equations for lead, it appears that the best is that given by Fischer,[1] viz.,

$$\mathrm{Pb}(l) = \mathrm{Pb}(g):$$

$$\log P = -\frac{10{,}250}{T} + 8{\cdot}549 - 1{\cdot}05 \log T \quad . \quad . \quad (1)$$

(P is in atm. and T in ° K.)

For the free energy of vaporisation of zinc, the equation given by Kelley[2] has been selected, viz.,

$$\mathrm{Zn}(l) = \mathrm{Zn}(g):$$

$$\Delta G^\circ = 30{,}902 + 6{\cdot}03T\log T + 0{\cdot}275 \times 10^{-3}T^2 - 45{\cdot}03T \quad . \quad (2)$$

where ΔG° is in cal.

On the heat of fusion of lead, the published calorimetric data are rather discordant. It appears that a more reliable value can be calculated from the course of the solidus and liquidus lines in binary systems containing lead. The best results for this purpose have proved to be the measurements of depression of freezing point carried out by Heycock and Neville.[3] Exhaustive testing of their results for thermodynamic consistency amongst themselves and with more recent data conclusively proves that the accuracy was as good as the authors claimed. The equation so deduced for the free energy of fusion of lead may be written as

$$\mathrm{Pb}(s) = \mathrm{Pb}(l):\ \Delta G_{600\cdot5} = 0;\ \Delta S = +\ 1{\cdot}81 \text{ cal./degree} \quad . \quad (3)$$

at 600·5° K.

This figure for the entropy of fusion is considerably lower than that generally quoted.

An examination of the calorimetric data and thermodynamic evidence on the heat of fusion of zinc has been made. The figure obtained in this case is in reasonably good agreement with those generally quoted:

$$\mathrm{Zn}(s) = \mathrm{Zn}(l):\ \Delta G_{692\cdot6} = 0;\ \Delta S = +\ 2{\cdot}51 \text{ cal./degree} \quad . \quad (4)$$

at 692·6° K.

The following equation is put forward to represent the change in free energy when 1 g.-atom of a liquid lead-zinc alloy is formed from its liquid components.

$$\Delta G = \boldsymbol{R}T(N_{\mathrm{Pb}}\ln N_{\mathrm{Pb}} + N_{\mathrm{Zn}}\ln N_{\mathrm{Zn}})$$

$$+ \frac{\sqrt{1{\cdot}6}\, N_{\mathrm{Pb}} N_{\mathrm{Zn}}}{1{\cdot}6 N_{\mathrm{Pb}} + N_{\mathrm{Zn}}}(5000 - 0{\cdot}52T) + \frac{\sqrt{3{\cdot}2}\, N_{\mathrm{Pb}} N_{\mathrm{Zn}}}{3{\cdot}2 N_{\mathrm{Pb}} + N_{\mathrm{Zn}}}(3215 - 2{\cdot}79T)$$

$$- \frac{1{\cdot}6^2 N_{\mathrm{Pb}}^2 N_{\mathrm{Zn}}^2}{8\boldsymbol{R}T(1{\cdot}6^{\frac{1}{2}} N_{\mathrm{Pb}} + N_{\mathrm{Zn}})^3}(5000 - 0{\cdot}52T)^2 \quad . \quad . \quad (5)$$

where N_{Pb} and N_{Zn} refer to mole fractions of Pb and Zn.

In eqn. (5) the first term is, of course, the ideal free energy of mixing. The second and third terms, it will be noticed, bear some resemblance to those used by Hildebrand[4] and others to represent departure from ideality for regular solutions. The usual volume fraction formula has been split into two terms to represent separately the effect of neighbouring and of more distant atoms. Another difference from the usual formulation is that allowance is made for non-ideal entropy of mixing attributable to the nature of the vibrational partition functions. The last term is the correction for departure from randomness of distribution of the atoms. For the present purpose, the theoretical basis for this formula is unimportant. The thesis of this paper is rather that, having determined the best self-consistent free-energy equation to agree with the most reliable data on a binary system, one is justified in deriving therefrom what may be regarded as the most accurate available values of all equilibrium properties of the system.

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[1] Fischer, *Z. anorg. Chem.*, 1931, **202**, 1.

[2] Kelley, *U.S. Bur. Mines, Bull.*, No. 383, 1935.

[3] Heycock and Neville, *J. Chem. Soc.*, 1892, **61**, 888.

[4] Hildebrand, *Solubility of Non-Electrolytes*, 2nd Edn. (1936).

For representing the properties of solid solutions of zinc in lead, the following equation, giving the change in free energy when 1 g.-atom of solid zinc is dissolved in lead, has been deduced.

$$\mathrm{Zn}(s) = \mathrm{Zn}(\mathrm{Pb}\ (s)) : \Delta G = 9720 - 5{\cdot}11T + RT\ln N_{\mathrm{Zn}} \quad . \quad (6)$$

From the above equations, the equilibrium relations in the lead-zinc system are calculated and represented graphically, for comparison with the published experimental results. For most of the phase diagram, the agreement between experimental points and calculated curves is as good as can be expected from the claimed accuracy of either. In some cases, to which attention is drawn, there are significant differences, and the values given by the curves are believed to be nearer the truth than the reported experimental results.

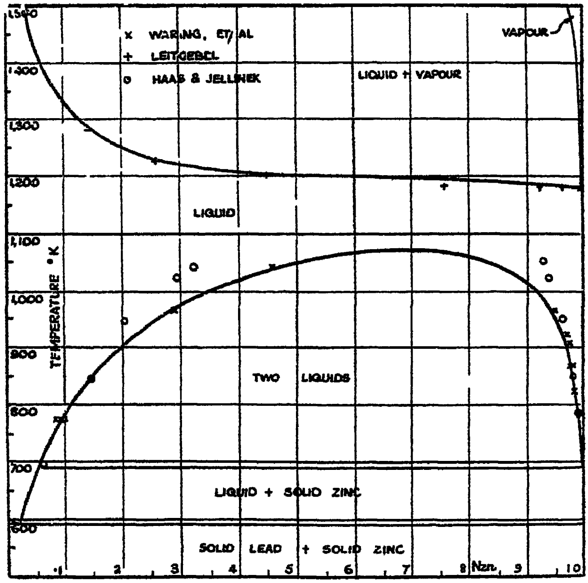

FIG 1.—The lead-zinc phase diagram at one atmosphere pressure

2. The Lead-Zinc Phase Diagram

Fig. 1 shows the lead-zinc phase diagram. The calculated normal boiling-point curve is generally in good agreement with the results of Leitgebel,[5] the biggest difference being at $N_{\mathrm{Zn}} = 0{\cdot}760$, where the experimental point is 1183° K., whereas the curve gives 1192° K. A boiling point of 1183° K. implies that the activity of the zinc is 0·97; an activity so near to unity at this temperature and composition is incompatible with other properties of the system, and confidence is felt that 1192° K. is a better estimate than 1183° K.

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[5] Leitgebel, *Z. anorg. Chem.*, 1931, **202**, 320.

On the miscibility gap the most reliable data are those of Waring and his collaborators.[6] It can be seen that the curve agrees well with their results over the entire range. They determined the temperature of complete miscibility as between 1043° K. and 1073° K.; the curve gives 1071° K. The results of Haas and Jellinek[7] are undoubtedly erroneous at the higher temperatures but agree with those of Waring below 900° K. Both sets of results are shown for the zinc-rich region in Fig. 2.

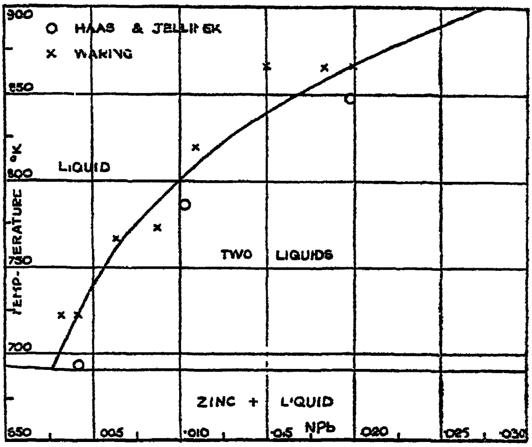

FIG. 2.—Solubility of lead in zinc.

Waring reports $N_{Zn} = 0{\cdot}9978$ for the monotectic composition; Haas and Jellinek report $N_{Zn} = 0{\cdot}9959$ for the zinc-rich phase at 693° K., just above the monotectic temperature. Waring's figure was deduced from his two results, shown in Fig. 3, on the zinc liquidus. These indicate that the liquidus is pronouncedly convex, which is extremely unlikely for such dilute solutions. The curve drawn, calculated from eqn. (4) and (5), differs very little from that which would be obtained were the activity of the zinc equal to its atomic fraction. This curve agrees almost exactly with the results of Heycock and Neville.[8] There is every reason to believe that the course of the liquidus,

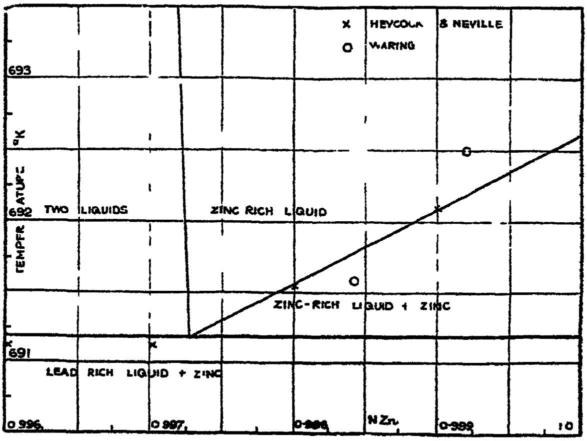

FIG. 3.—The zinc-rich liquidus.

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[6] Waring, Anderson, Springer and Wilcox, *Trans. Amer. Inst. Min. Met. Eng.*, 1934, **111**, 254.

[7] Haas and Jellinek, *Z. anorg. Chem.*, 1933, **212**, 356.

[8] Heycock and Neville, *J. Chem. Soc.*, 1897, **71**, 383.

as drawn, is substantially correct. According to Waring, the monotectic temperature is 1·6° K. below the melting point of zinc ; Heycock and Neville find 1·5° K. for this difference. Fig. 3 takes the monotectic temperature as 1·42° K. below the melting point of zinc and gives the monotectic composition as $N_{Zn} = 0{\cdot}9973$.

For the solubility of zinc in liquid lead at the monotectic temperature, Haas and Jellinek find $N_{Zn} = 0{\cdot}061$, while Waring reports an identical figure, apparently, however, obtained only by extrapolation from his other results. The calculated figure of $N_{Zn} = 0{\cdot}052$, as given by the curve of Fig. 1, is believed to be nearer the truth.

For the lead-rich eutectic composition, Hodge and Heyer[9] report $N_{Zn} = 0{\cdot}0157$, a figure with which Waring agrees exactly without giving experimental details. Hodge and Heyer obtained their result as the composition at which the curve passing through the liquidus points which they determined intersects the eutectic temperature line. As can be seen from Fig. 4, their points indicate a convex liquidus, whereas the calculated curve is slightly concave. Here again the results of Heycock and Neville[3] fit excellently a thermodynamically self-consistent curve, about which it is reasonable to regard the results of Hodge and Heyer as randomly scattered. Heycock and Neville found a eutectic temperature 9·08° K. below the melting point of lead, while Hodge and Heyer found 9·2° K. Fig. 4 shows this temperature interval as 9·05° K.; this implies a eutectic composition of $N_{Zn} = 0{\cdot}0181$, which appears to be consistent with the microscopic evidence presented by Hodge and Heyer.

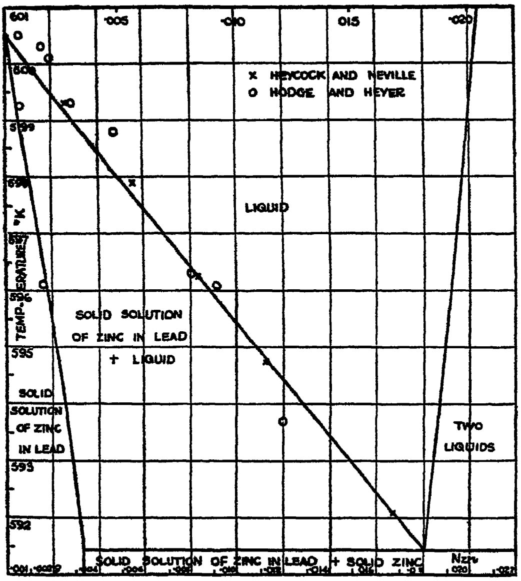

FIG 4.—The lead-rich liquidus.

As shown in Fig. 4, Hodge and Heyer fixed two points on the lead-rich solidus from halts on heating curves. From the absence of a eutectic break on cooling curves at $N_{Zn} = 0{\cdot}0016$ and the presence of a eutectic break at $N_{Zn} = 0{\cdot}0019$, they concluded that the solid solubility at the eutectic temperature is about $N_{Zn} = 0{\cdot}0016$. This evidence appears to be rather inconclusive. Eqn. (6), on which the solidus curve shown is based, was deduced so as to be thermodynamically consistent with the liquidus curve of Heycock and Neville. This leads to quite good agreement with the two solidus points determined by Hodge and Heyer, but gives a solid solubility at the eutectic temperature of $N_{Zn} = 0{\cdot}0033$; this figure is believed to be the best estimate possible with the available experimental data. From eqn. (6) the solid solubility curve below the eutectic temperature can be calculated, as shown in Fig. 5; there are no published results for confirming this.

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[9] Hodge and Heyer, *Met. Alloys*, 1931, 5, 297.

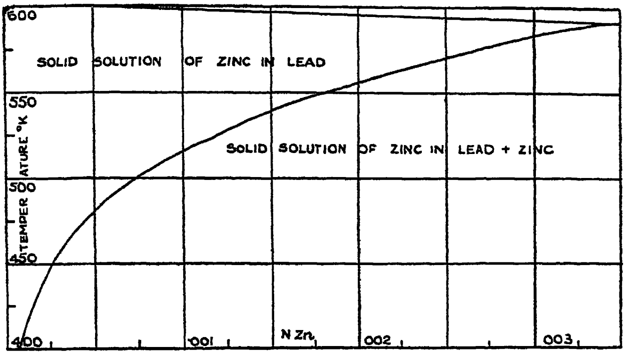

FIG. 5 —Calculated solid solubility of zinc in lead.

3. Heat of Mixing

The heat of mixing of zinc and lead is implicit in eqn. (5). In Fig. 6, the full curve represents the calculated heat of mixing for 723° K. and the points the experimental results of Kawakami[10] for 723° K. The agreement is rather poor. There is a better agreement between the experimental results and the calculated curve, shown as a broken line, for 703° K., but there still remains a large discrepancy for the result at $N_{Zn} = 0{\cdot}070$. Drawing a line from the origin through this point at $N_{Zn} = 0{\cdot}070$ to intersect the line through the points for the miscibility gap would imply that at 723° K. a saturated solution of zinc in lead has a composition in the region of $N_{Zn} = 0{\cdot}17$; from the experimental points shown in Fig. 1, it is clear that

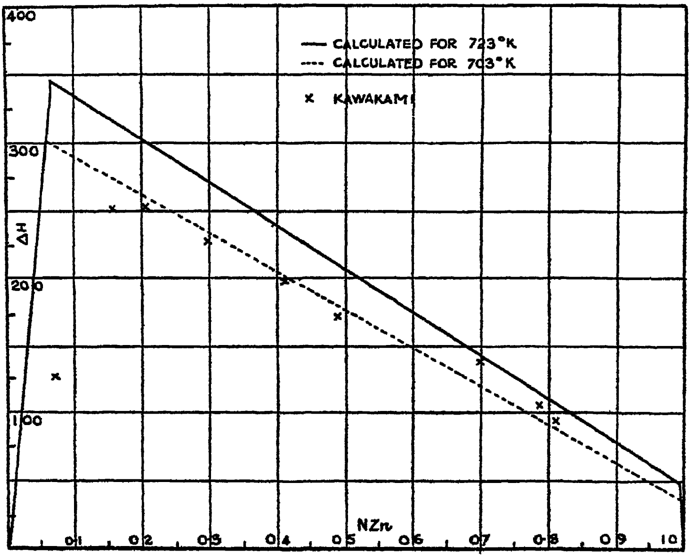

FIG. 6.—The heat of mixing of zinc and lead.

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[10] Kawakami, *Z. anorg. Chem.*, 1927, 167, 345.

this is incorrect. If, as thus seems certain, Kawakami's result for $N_{Zn} = 0{\cdot}070$ is seriously in error, no high accuracy can be ascribed to his other results. It is therefore believed that the calculated curve shown for 723° K. is more accurate than one drawn simply to fit Kawakami's results.

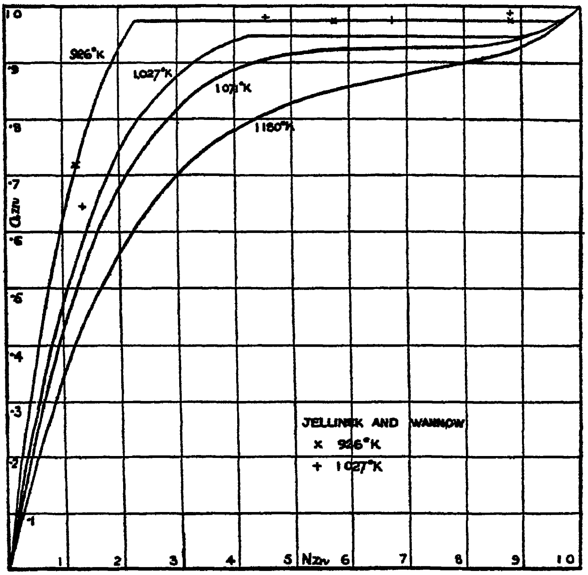

FIG. 7.—The activity of zinc in its liquid alloys with lead.

4. Activities and Vapour Pressures

In Fig. 7 are plotted the zinc activity curves for 926° K., 1027° K., 1071° K., and 1180° K. At the two lower temperatures a comparison can be made with the vapour pressure measurements of Jellinek and Wannow.[11] At 926° K. the agreement is perfect; at 1027° K. the difference for $N_{Zn} = 0{\cdot}135$ appears to be within the admitted error of the experimental results. 1071° K. is the minimum temperature of complete miscibility, and the curve becomes practically horizontal between $N_{Zn} = 0{\cdot}6$ and $N_{Zn} = 0{\cdot}8$. At 1180° K., the boiling point of zinc, the curve never becomes horizontal, but the activity of the zinc decreases only from 0·93 to 0·83 as N_{Zn} decreases from 0·9 to 0·5; consequently, in this range, the boiling-point curve, as shown in Fig. 1, is very flat.

The boundary of the vapour phase at one atmosphere pressure is indicated in Fig. 1, but, except at the higher temperatures, the lead concentration is too small to be conveniently represented there. Fig. 8 shows the lead content of the vapour, as a function of liquid composition, for alloys at their normal boiling points. This curve starts off from the origin with a slope,

$$\frac{N_{Pb}(g)}{N_{Pb}(l)} = 0{\cdot}0041.$$

That is, for dilute solutions of lead in zinc at 1180° K., the gas phase contains 0·0041 times as much lead as the liquid.

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[11] Jellinek and Wannow, *Z. Elektrochem.*, 1935, **41**, 346.

5. Applications to Process Metallurgy

A quantitative knowledge of the activities of zinc and lead in their liquid alloys is of help in explaining the extent to which lead is volatilised during the operations of zinc smelting. In the intermittent, horizontal-retort smelting process, where the gases produced consist of equal volumes of zinc and carbon monoxide, it can readily be shown that the lead in the charge is present as metal, with its activity reduced very little below unity by the zinc dissolved in it. The concentration of lead in the vapour is therefore determined essentially by the vapour pressure of lead at the temperature of the charge in the retort. The percentage of lead in the zinc produced at each stage of the distillation is therefore independent of the amount of lead present in the charge, provided that, as is usually the case, there is sufficient lead there to saturate the gas throughout the cycle of operations. The temperature, and hence the lead content of the zinc condensed, increases as the distillation proceeds. If, however, the material treated contains very little lead, the first zinc distilled off contains approximately the normal amount of lead; then the lead in the charge becomes exhausted, so that the later metal tapped is comparatively free from lead. It is customary to liquate high-lead zinc obtained from horizontal retorts; the extent to which the lead content can be reduced is illustrated in Fig. 3.

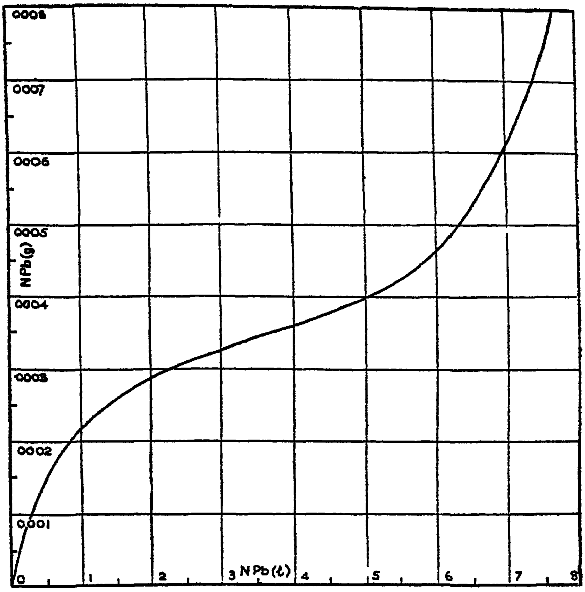

Fig. 8.—Composition of the vapour from boiling lead-zinc alloys.

In the more modern, continuously operated, vertical retorts, the mixture of zinc vapour and carbon monoxide passes through an unheated extension of the retort, which is filled with briquetted charge. Here the gases are slightly cooled, but necessarily their temperature cannot fall below 1115° K., the zinc dew-point. At this temperature the vapour pressure of lead is such as to give 0·09 % lead in the zinc. In the usual practice, the zinc produced contains somewhat over 0·1 % lead.

High purity zinc, needed for making zinc-aluminium die-casting alloys, is produced by distilling and refluxing the crude metal. The boiling-point curve of Fig. 1 and the relation between the lead content of liquid and vapour, as given in Fig. 8, can be used to calculate the purification attainable under various conditions.

It may be of some interest to mention a recently developed American process[12] for dezincing desilverised lead by vacuum distillation. Lead containing 0·5–0·6 % zinc is heated to 600° C. and the pressure reduced to 0·5 mm. Hg. Within about 2 hr. the pressure has dropped to 0·05 mm. Hg., at which figure it remains for the rest of the 5-hr. distillation period. The partial pressure of the zinc under such conditions can be calculated from the data given in the present paper.

Summary

From the available experimental data on the lead-zinc system, an equation to represent the free energy of mixing of liquid zinc and lead has been derived. Hence a thermodynamically self-consistent phase diagram is drawn. The manner in which these calculations may be applied to problems in zinc smelting and refining is indicated.

It is calculated that the entropy of fusion of lead is 1·81 cal. ° c.$^{-1}$ g.-atom.$^{-1}$. At the lead-zinc monotectic, the atomic fractions of zinc in the two liquid phases are estimated to be $N_{Zn} = 0·052$ and $N_{Zn} = 0·9973$. For the eutectic, the calculated composition of the liquid is $N_{Zn} = 0·0181$, the solubility of zinc in solid lead at the eutectic temperature being $N_{Zn} = 0·0033$.

Research Department,
National Smelting Co. Ltd.,
Avonmouth.

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[12] Isbell, *Met. Tech.*, 1947, **14**, T.P. 2138.

ASPECTS OF GAS-METAL EQUILIBRIUM, INTERSTITIAL SOLUTION AND DIFFUSION

BY R. M. BARRER

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Several non-metallic elements which play fundamental roles in metallurgical processes may enter the lattice of a metallic crystal to give interstitial solid solutions. The properties of many of these phases are remarkable and despite progress already made,[1 2 3] much remains to be done in interpreting them. Some features of such phases will, therefore, be reviewed from the standpoints of crystal chemistry, interatomic forces, equilibria, and kinetics of formation.

(1) Conditions for Formation of Interstitial Phases

Elements usually from the first short series (H, B, C, N and O), sometimes form zeolitic solid solutions in metals of the transition series. For such a reaction to occur, the free energy of the solution must be less than that of the original metallic crystal and of the non-metallic phase. The subsequent decrease of free energy on solution must also be greater than that for any other phases which might also form (oxides, nitrides, carbides, etc.). These

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[1] Häag, *Z. physik. Chem. B*, 1929, **6**, 221 ; *Z. physik. Chem.*, 1930, **7**, 339 ; *Z. physik. Chem.*, 1930, **8**, 445 ; *Z. physik. Chem.*, 1931, **12**, 33.

[2] Rundle, Baenziger, Wilson, and McDonald, *J. Amer. Chem. Soc.*, 1948, **70**, 99.

[3] Horn and Ziegler, *J. Amer. Chem. Soc.*, 1947, **69**, 2372.

TABLE I

Some Radius Ratios for Metals and Non-Metals *

Metal			Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zr	Cb	Mo	Ru	Rh	Pd	Ag	Th	U
Non-metal	Radius in A.	Radius in A. for C.N. 12	1·467	1·338	1·357 1·267	1·306 1·261	1·260	1·252	1·244	1·276	1·597	1·456	1·386	1·366	1·342	1·373	1·442	1·795	1·516
H (C.N. = 4)	0·48	Radius Ratios	0·33	0·36	0·35 0·38	0·37 0·38	0·38	0·38	0·39	0·38	0·30	0·33	0·35	0·35	0·36	0·35	0·33	0·27	0·32
Be (C.N. = 6)	1·033		0·71	0·77	0·76 0·82	0·79 0·82	0·82	0·83	0·83	0·81	0·65	0·71	0·75	0·76	0·77	0·75	0·72	0·58	0·68
B (C.N. = 6)	0·89		0·61	0·66	0·66 0·70	0·68 0·71	0·71	0·71	0·72	0·70	0·56	0·61	0·64	0·65	0·66	0·65	0·62	0·50	0·59
C (C.N. = 6)	0·824		0·56	0·62	0·61 0·65	0·63 0·65	0·65	0·66	0·66	0·65	0·52	0·57	0·59	0·60	0·61	0·60	0·57	0·46	0·54
N (C.N. = 6)	0·79		0·54	0·59	0·58 0·62	0·61 0·63	0·63	0·63	0·64	0·62	0·49	0·54	0·57	0·56	0·59	0·57	0·55	0·44	0·52
O (C.N. = 6)	0·803		0·55	0·60	0·59 0·63	0·62 0·64	0·64	0·64	0·65	0·63	0·50	0·55	0·58	0·59	0·60	0·59	0·56	0·45	0·53
F (C.N. = 6)	0·87		0·59	0·65	0·64 0·69	0·67 0·69	0·69	0·69	0·70	0·68	0·54	0·60	0·63	0·64	0·65	0·63	0·60	0·48	0·57

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* The radii given are due to Pauling.[4] The radius for oxygen for C.N. = 6 is derived by adding 0·143 A. to the single-bonded oxygen radius of 0·66 A., using formula (3) of Pauling's paper, with n for divalent oxygen in sixfold co-ordination = $\frac{1}{3}$. A similar correction for fluorine (valence 1, C.N. = 6) is $0{\cdot}23_4$ A. giving 0·87 A. for the corrected radius, while for H (C.N. = 4, valence 1) the corrected radius is 0·48 A.

requirements are sometimes fulfilled since interstitial solutions are well known.

A geometrical consideration contributes to the free-energy change in forming an interstitial solution. The radius ratio of the non-metallic element, X, to the metallic one, A, must be small ($<$0·59[*]) for only then will X occupy interstices in A without undue distortion of the parent lattice of A. In such an ideal interstitial solution the metal atoms still remain in contact, and their arrangement is unaltered, i.e., is mainly cubic or hexagonal close-packed (co-ordination number 12) or body-centred cubic (co-ordination number 8). When the radius ratio approaches or slightly exceeds the critical value of 0·59, distortion of the lattice of A becomes increasingly evident, and the phase may break down into one or more non-interstitial compounds as the content of X increases.

Table I summarises some radius ratios for elements of the first short series and a number of the transition elements. The radii[4] are corrected for the co-ordination number (C.N.) of the element. This can only be partially done for the metals because, for example, the C.N. of 12 rises as the content of X increases until in a phase AX of rock salt structure (i.e., 12 A–A contacts and 6 A–X contacts per atom of A) the C.N. is 18 for each atom A.[†] On the other hand the valence of the metal *may* increase and this would tend to offset the effect of co-ordination upon the metallic radii.[4] [5] Metallic radii for C.N. = 12 have been used throughout the table, and the radius ratios are probably upper limits. These ratios are in fact slightly greater than some previously given.[6]

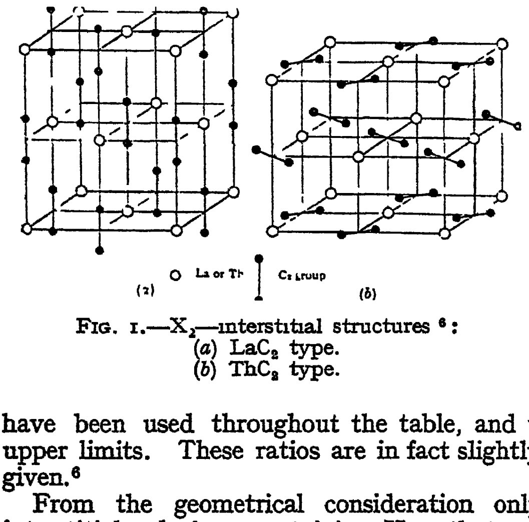

FIG. 1.—X$_2$—interstitial structures[6]:
(*a*) LaC$_2$ type.
(*b*) ThC$_2$ type.

From the geometrical consideration only, one would expect many interstitial solutions containing H; that such phases containing C, N or O should be common; while interstitial B or F would not often occur, and interstitial Be should be a rarity. Such considerations alone are inadequate because a second factor comes into play—the electronegativity difference between A and X. Thus for example F, very high in the electronegativity scale, always forms ionic fluoride lattices with metals. The electronegativities decrease in the sequence F(4·0)$>$O(3·5)$>$N(3·0)$>$

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[4] Pauling, *J. Amer. Chem. Soc.*, 1947, **69**, 542.

[5] Pauling, *Physic. Rev.*, 1938, **54**, 899.

[6] cf. Evans, *Crystal Chemistry* (C.U.P., 1939)., 148.

[*] The upper limit 0·59 corresponds to the radius ratio near which octahedral co-ordination of X becomes unstable relative to a special structure where X has a co-ordination number = 7. When the ratio reaches 0·65 another special structure where X has a co-ordination number = 8 might be expected. Unless such interstitial structures do occur in sequence the upper limit 0·59 must be only a rough approximation. Indeed for all radius ratios above 0·41, expansion or distortion of the metal lattice is likely for octahedral co-ordination of X.

[†] Similarly in interstitial solutions AX$_2$ of fluorite structure there are 12 A-A and 8 AX contacts per metallic atom for which the C.N. is then 20. In zinc-blende type solutions, A-X, the C.N. for A is 16 (12 A-A contacts and 4 A-X contacts).

C(2·5) > H(2·1), so that the interference of this factor with the geometrical criterion should decrease in the same order. These electronegativities may be compared with 1·6 for Ti and Zr and 1·3 for Sc and Y, as typical transition elements.[7]

In a close-packed array of metal atoms two kinds of interstitial position occur: " octahedral " sites (C.N. = 6); and " tetrahedral " sites (C.N. = 4). Which kind of site X will occupy depends on the rule that it attains the highest co-ordination number compatible with its size. Larger atoms X tend, then, to occupy octahedral sites and smaller ones the tetrahedral sites, the maximum radius ratio being about 0·59 for C.N. = 6 and 0·41 for C.N. = 4. There is no need for all the sites of a given type to be filled because the metal lattice is stable in the absence of any interstitial atoms. However, since there is only a limited number of sites the composition cannot go past a specific upper limit. Thus for the atom X in octahedral co-ordination, a sodium chloride type of structure of composition AX is the anticipated limit. In fourfold co-ordination, complete filling of all sites may give a fluorite structure of composition AX_2, while the symmetrical filling of one half of these sites may give a zinc-blende structure of composition AX.

TABLE II

CRYSTAL CHEMICAL DATA ON SOME INTERSTITIAL SOLUTIONS

Co-ordination of Atoms X	Proportion of X sites occupied	Arrangement of metal Atoms A in phase	Structure of phase	Examples
Sixfold (0·41–0·59) radius ratio	1·0	Cubic close-packed	Rock salt	TiC, ZrC, HfC, ThC, TiN, ZrN, ScN, VC, NbC, TaC, VN, CrN
	0·5	„	„	W_2N, Mo_2N
	0·25	„	„	Mn_4N, Fe_4N
Fourfold (0·23–0·41) radius ratio	1·0	Cubic close-packed	Fluorite	TiH_2
	0·5	„	Zinc-blende	ZrH, TiH
	0·25	„	„	Pd_2H
	0·125	„	„	Zr_4H
Sixfold (0·41–0·59) radius ratio	0·25	Hexagonal close-packed	—	Ta_2C, V_2C, W_2C, Mo_2C, Mn_2N, Cr_2N, Fe_2N
Fourfold (0·23–0·41) radius ratio	0·25	Hexagonal close-packed	Wurtzite	Zr_2H, Ta_2H, Ti_2H
Fourfold (>0·29) radius ratio	—	Body-centred cubic	—	TaH
Sixfold (>0·58) radius ratio	—	Simple hexagonal	—	WC, MoN

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[7] Pauling, *Nature of the Chemical Bond* (Cornell Univ. Press, 1940), p. 64.

A classification of some interstitial structures is given in Table II. In addition there are the so-called X_2 structures in which the atoms X, notably carbon, occur in pairs. Such are the phases LaC_2, CeC_2, PrC_2, NdC_2, UC_2, and VC, conforming to one variant, and ThC_2 and ZrC_2 conforming to a second variant of an arrangement of X_2 groups in sixfold co-ordination in the interstices of a somewhat distorted simple cubic lattice (Fig. 1).[8]

TABLE III

Phase Composition	M.p. ° K.	Hardness (Moh's Scale)
TiC	3410	8–9
HfC	4160	—
W_2C	3130	9–10
NbC	3770	—
ZrB	3265	9
TiN	3220	8–9
ZrN	3255	8
TaN	3360	—

In addition to the phases of Table II, interstitial borides are known, and an interstitial solution of oxygen in Zr with a limiting composition[9] of about $ZrO_{0\cdot4}$ and of oxygen in Ti with about 42 atoms % of oxygen.[10] The interstitial structures have many metallic properties (opacity, metallic lustre, electronic conductivity, super-conductivity [8]). In addition, they sometimes possess the very valuable properties of inertness, great hardness and high m.p. (Table III).

(2) Nature of Interactions between Metal and Interstitial Atoms

The hydrogen atom is the smallest found in an interstitial solution. Because it is a gas, the properties of hydrogen-metal systems may be studied by techniques used for the measurement of sorption equilibria. An empirical classification of the interstitial solutions is possible,[11] into those formed endothermally (H in Fe, Co, Ni, Cu, Pt) and those formed exothermally (H in Pd, V, Ta, Ti, Zr, Th). For the first group of alloys the hydrogen solubility increases as the temperature rises; for the latter it increases as the temperature decreases, reaching limiting compositions at sufficiently low temperature or high hydrogen pressure (Fig. 2). From the variation of these solubilities with temperature approximate sorption heats (ΔH) may be derived which are given in Table IV, both for 1 g. mol. of *molecular* hydrogen, and for 1 g. atom of *atomic* hydrogen. Referred to hydrogen atoms, the transfer from gas phase to these metallic interstices is always strongly exothermal, and the magnitude of the interaction is so large as to suggest forces other than

TABLE IV

HEATS OF SOLUTION OF HYDROGEN IN METALS

Metal	Heat of Solution in cal./mol. of H_2	Heat of Solution of 1 g. atom of H atoms (cal.)
Ti	−10,000	−56,000
Zr	−17,500	−59,800
Th	−22,500	−62,300
V	− 7,700	−54,900
Pd	− 2,040	−52,000
Cu	+14,100	−44,000
Co	+ 7,300	−47,400
Fe	+ 7,000	−47,500
Ni	+ 5,600	−48,200
Pt	+35,400	−33,300
Mo	+ 3,500	−49,300

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[8] After Evans, ref. 6, Fig. 33.

[9] de Boer and Fast, *Rec. trav. chim.*, 1940, 59, 161.

[10] Ehrlich, *Z. Elektrochem.*, 1939, 45, 362.

[11] cf. Barrer, *Diffusion in and through Solids* (C.U.P., 1941), p. 151.

van der Waals' cohesion between hydrogen atoms in their interstitial environment and neighbouring metal atoms.

Several views are possible as to the nature of the interaction. The transition metals are often paramagnetic, a phenomenon usually ascribed to unshared electrons or " positive holes " in the *d*-levels. Crystals of Ni or Pd, for instance, have about 0·6 unpaired electrons per atom. Progressive replacement of Ni (at. no. = 28) by Cu (at. no. = 29) in a *substitutive* solid solution results in an increase in the total electrons available, and the additional electrons will tend to go into states of lowest energy, here into the unfilled *d*-levels. At the composition $Cu_{0 \cdot 6}Ni_{0 \cdot 4}$, 0·6 extra electrons per atom have entered the crystal, the paramagnetism of which is then found to be zero. Similarly when H enters the Pd lattice, at the composition $PdH_{0 \cdot 6}$, 0·6 extra electrons per Pd atom have been added, and if these enter the unfilled *d*-levels the phase will, as observed, be paramagnetic and a limit set to its H content.[12] Such a view, while describing adequately composition limits and magnetic properties, would suggest that the H atoms are actually present as cations. Efforts to demonstrate the presence of cationic hydrogen have at best, however, had limited success.[13] Thus although the H in Pd drifts towards the cathode under an applied P.D., the estimated positive charge per atom is only a small fraction of the proton charge. An alternative view is that only one H atom out of many exists as a proton. In either view the interstitial hydrogen is to be regarded as substantially unionised.

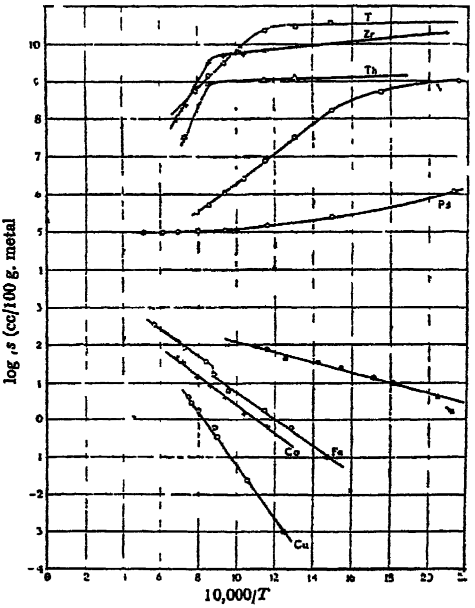

FIG. 2.—Temperature variation of solubility at 1 atm. pressure of hydrogen in metals dissolving it exothermally and endothermally.[15]

A further weakness of the above view if applied to other interstitial structures is that it does not easily explain the hardness and inertness of many of these phases. A chemical explanation involving valence bonds between the metallic atoms and between metallic and interstitial atoms may do this much better if the metallic characteristics can also be preserved. Such a view of the metallic state in general has been developed by Pauling,[4, 5] which takes over for metal crystals the theory of the electron-pair bond, hybridisation of " pure " *d*, *s*, and *p* orbitals, and resonance. A not dissimilar view of the hydride UH_3 has been given by Rundle.[14] Here the structure is more complex than that of a simple interstitial hydride, although metallic conductivity remains.

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[12] Emeleus and Anderson, *Modern Aspects of Inorganic Chemistry* (Routledge, 1938), p. 446.

[13] Coehn and Specht, *Z. Physik*, 1930, **62**, 1. Duhm, *Z. Physik*, 1935, **94**, 434.

[14] Rundle, *J. Amer. Chem. Soc.*, 1947, **69**, 1719.

[15] Smithells and Fowler, *Proc. Roy. Soc. A*, 1937, **160**, 38.

For a chemical explanation of the inertness and hardness of many interstitial structures, the most important property is the very great number of potentially bond-forming contacts between metal atoms and between metal and non-metal atoms. This number of contacts is unequalled in any substitutional solid solution. The number of electrons per atom available to form electron pair bonds is always less than the number of contacts per atom, and so the bonds formed will be fractional ones, resonating among the available positions. The resonance energy increases further the stability of the phase, while the resonance of valence electrons throughout the crystal confers on it the property of metallic conductivity.

The interstitial atoms which enter the parent metal crystal also supply electrons available for bond formation (H contributes 1; B, 3; C, 4; N, 3 (or 5); O, 2 (4 or 6).* In the parent metal crystal, for example, Fe, Co, or Ni, there are on Pauling's theory 5·78 valence bonds per atom; and 2·22, 1·71, and 0·61 unpaired *d*-electrons respectively per atom. The 5·78 valence bonds per atom are attributed to *dsp* hybridisation, involving 2·56 *d*-orbitals, 1·0 *s*-orbitals and 2·22 *p*-orbitals. Introduction of interstitial atoms may modify the hybridisation of the "pure" orbitals in the metallic atoms; or may use separately the unpaired electrons referred to above. Various possibilities can thus arise, but without further magnetic and other experimental data it would be out of place to attempt an analysis. One may, however, briefly interpret the Pd-H phase according to this view. In Pd the situation corresponds to that in Ni. In the pure metal there are 5·78 valence electrons used per atom (2·56*d*, 1·0*s*, and 2·22*p*). There are also 0·60 unpaired 4*d*-electrons and 3·62 paired non-bonding 4*d*-electrons per atom. When H-atoms enter the crystal the unpaired *d*-electrons are, on the chemical theory, progressively used up in forming electron-pair bonds with the 1*s*-electron of the H atom. This may be done in several ways, one of which involves promotion of an unpaired 4*d*-electron to the 5*p*-orbital at the moment of bond formation. In any case when the composition $PdH_{0\cdot6}$ is reached, the *d*-electrons are used up and so more hydrogen can enter the crystal. Also the crystal should have zero paramagnetism. Both features are in agreement with experiment.

(3) Interstitial Sorption Equilibrium

Equilibrium between a gas sorbed interstitially and the free gas may be formulated statistically.[15] [16] [17] Such treatments usually regard the medium as providing a uniform set of sites which are occupied by atoms or molecules of the gas.

Consider the distribution of a gas between a gas volume V_g and an interstitial volume V_i. In the gas phase containing N_g molecules, the free energy per molecule, $\frac{A_g}{N_g}$, is:

$$\frac{A_g}{N_g} = kT\ln\left(\frac{N_g}{eV_g} \cdot \frac{h^3}{(2\pi mkT)^{3/2}}\right) = kT\ln\left(\frac{p}{ekT} \cdot \frac{h^3}{(2\pi mkT)^{3/2}}\right) \quad . \quad (1)$$

where h = Planck's constant, k = Boltzmann's constant, m = the mass of the molecule, and $j_g(T)$ = the partition function for rotational and vibrational degrees of freedom of the molecule. In the interstitial volume, when a fraction θ of all the available sorption sites is occupied by N_i interstitial molecules, the free energy of a sorbed molecule is

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[16] Lacher, *Proc. Roy. Soc. A*, 1937, **161**, 525.

[17] Barrer, *Trans Faraday Soc.*, 1944, **40**, 374.

* The numbers of additional electron pair bonds would thus be larger for B, C, and N than for H, and the interstitial structures might therefore be harder for B, C, and N, as is observed.

$$\frac{A_i}{N_i} = kT \,.\, \ln\left(\frac{\theta}{1-\theta} \cdot \frac{1}{a_i(T)}\right) \quad . \quad . \quad . \quad . \quad (2)$$

where $a_i(T) = ej_i(T) \,.\, e^{\frac{\varphi}{kT}}$ is the partition function for an occluded molecule, φ is the least energy needed to remove a molecule from the interstitial to the gas volume, and $j_i(T)$ is the partition function for internal degrees of freedom of the molecule and its motions relative to the lattice. If the molecule behaves interstitially as an oscillator vibrating with mean frequency ν, and internal degrees of freedom (including rotations) remain the same as for a gaseous molecule, then

$$j_i(T) \simeq \left(\frac{kT}{h\nu}\right)^3 j_g(T) \quad . \quad . \quad . \quad . \quad . \quad (3)$$

At equilibrium the free energy of a gas molecule in both phases must be the same, so that *

$$\frac{\theta}{p(1-\theta)} = K_1 = \frac{1}{kT}\left(\frac{kT}{2\pi m}\right)^{3/2} \frac{1}{\nu^3} e^{\frac{\varphi}{kT}} \quad . \quad . \quad . \quad (4)$$

Eqn. (4) applies to the distribution, for example, of *atomic* hydrogen between gas phase and metallic interstices. For the hydrogen *molecules* in equilibrium with atoms

$$H_2 \rightleftharpoons 2H \,; \;\; K_2 = \frac{[H]^2}{[H_2]},$$

where values of K_2 can be obtained in the range 500°–2500° K. from the relation[19]

$$K_2 = K_0 e^{-\frac{\Delta U}{RT}} = 10^{5.57}\, e^{\frac{-101{,}000}{RT}} \quad . \quad . \quad . \quad (5)$$

Thus, substituting $p_H = \sqrt{p_{H_2} K_2}$ in eqn. (4),

$$\frac{\theta}{(1-\theta)\sqrt{p_{H_2}}} = K_1\sqrt{K_2} = K_1 10^{2.78}\, e^{\frac{-50{,}500}{RT}} \quad . \quad . \quad (6)$$

Some equilibria between gaseous and interstitial hydrogen have led to experimental entropies of occlusion very near to those calculated from eqn. (6), where the value of K_1 is taken to be that for oscillators. Free energies of occlusion can be quite well estimated using measured heats of occlusion and entropies of occlusion characteristic of oscillators.[17]

It may happen that at suitably high temperatures the oscillators become mobile. Values of K_1 were, therefore, calculated assuming three-dimensional translational mobility of the sorbate within the interstitial volume, two-dimensional translational mobility, and one-dimensional translational mobility respectively. Entropies of occlusion computed for each model suggested very different entropy " levels " corresponding to the different

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[18] Frenkel, *Kinetic Theory of Liquids* (O.U P., 1946), p. 171.
[19] Roberts, *Some Problems in Adsorption* (C.U.P., 1939), p. 59.

* If the oscillators were truly localised, the term on the right-hand side of eqn. (4) would contain an extra " e." However, as pointed out by Frenkel[18] in a discussion of the origin of the entropy of fusion, in *real* crystals as distinct from ideal ones, the term does not arise. This is because, in the present system the oscillators have a residual mobility which allows them occasionally to migrate from one interstitial site to another, so that the whole interstitial volume becomes available to each molecule, just as in a liquid or gas the whole free volume is also available.

degrees of interstitial mobility, so that experimental entropies of occlusion may offer a good guide as to interstitial mobility.[17]

The entropy levels are, however, less widely spaced than was originally thought, although the effect is large enough to remain a good measure of mobility of a sorbed phase.* Suppose the interstitial gas has gas-like mobility in the interstitial volume. Allowing for the high concentration in the interstitial solution, the volume available for the sorbed gas is $V_i\left(1 - \frac{N_i}{N_s}\right) = V_i(1 - \theta)$ where N_s is the number of sorbate molecules needed to occupy all the sorption volume V_i. The partition function for the sorbed gas is then

$$Q_i = \left\{\frac{(2\pi mkT)^{3/2}}{h^3} \cdot V_i(1 - \theta) \cdot j(T)\, e^{\frac{\varphi}{kT}}\right\}^{N_i} \frac{1}{N_i!} \quad . \quad . \quad (7)$$

which, using Stirling's theorem, and setting $\theta = \frac{N_i}{N_s}$, leads to

$$\frac{A_i}{N_i} = kT \,.\, \ln\left(\frac{\theta}{1 - \theta} \cdot \frac{N_s}{V_i} \cdot \frac{h^3}{(2\pi mkT)^{3/2}} \cdot \frac{1}{e\,j(T)} \cdot e^{\frac{\varphi}{kT}}\right) \quad . \quad (8)$$

At equilibrium (i.e., equating eqn. (8) and (1)) one has

$$\frac{\theta}{(1 - \theta)p} = K_3 = \frac{1}{kT}\left(\frac{V_i}{N_s}\right) e^{\frac{\varphi}{kT}} = \frac{1}{kT} \cdot \frac{1}{N'_s} \cdot e^{\frac{\varphi}{kT}} \quad . \quad . \quad (9)$$

where N'_s is the number of molecules required to saturate 1 cc. of interstitial volume. Similarly, if there are two translational and one vibrational degrees of freedom for the sorbed molecule corresponding to complete mobility on internal surfaces,

$$\frac{\theta}{(1 - \theta)p} = K_4 = \frac{1}{kT}\left(\frac{kT}{2\pi m}\right)^{1/2} \cdot \frac{1}{\nu} \cdot \frac{1}{N''_s} \cdot e^{\frac{\varphi}{kT}} \quad . \quad . \quad (10)$$

where N''_s is the number of sorbate molecules required to saturate 1 cm.^{2} of internal surface. For one translational and two vibrational degrees of freedom of the sorbed molecule

$$\frac{\theta}{(1 - \theta)p} = K_5 = \frac{1}{kT} \cdot \left(\frac{kT}{2\pi m}\right) \cdot \frac{1}{\nu^2} \cdot \frac{1}{N'''_s} \cdot e^{\frac{\varphi}{kT}} \quad . \quad . \quad (11)$$

where N'''_s is the number of sorbate molecules per cm. at saturation. N'_s, N''_s and N'''_s were omitted from the original formulæ for K_3, K_4 and K_5; they will have values of the order 10^{22}, 10^{14} and 10^7 for small molecules and the change in entropy when an oscillator becomes fully mobile is then about 16 cal./degree.

A characteristic feature of some hydrogen alloys is that at a certain charge of gas the system becomes, or tends to become, univariant so that, on fixing the temperature, hydrogen is taken up at constant pressure. This behaviour has been discussed by Lacher [18] for the Pd–H_2 system. An attraction was postulated between interstitial hydrogen atoms which increased as θ increased (and so, on an average, the H atoms came nearer to one another). At a critical concentration, H atoms tend to cluster, yielding a hydrogen-rich phase in equilibrium with a hydrogen-poor phase. At this point, further charging of the metal with hydrogen merely increases the amount of hydrogen-rich phase at the expense of the hydrogen-poor phase, the pressure remaining constant.

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* A discussion with Dr. C. Kemball brought this point to the notice of the writer.

The assumption of an interaction between hydrogen atoms is reasonable. Each H atom is in fourfold co-ordination with Pd, in a "tetrahedral" site, and no two hydrogen atoms approach nearer to one another than corresponds to the distance between successive interstices. This, however, is quite small, so that an attraction is possible. Lacher's view is *not* compatible with the occurrence of hydrogen as protons which would always *repel* one another. The presence of hydrogen sometimes modifies the packing of the metallic atoms:

Phase	Ti_2H	TiH	TiH_2	Ta_2H	TaH
Packing of Metal Atoms.	H.c.p.	C.c.p.	C.c.p.	H.c.p.	B.c.c.

(H.c.p. = hexagonal close-packing; C.c.p. = cubic close-packing; B.c.c. = Body-centred cubic packing.) Such rearrangements may then also result in two phases.

(4) Kinetics and Non-equilibrium Processes

The rate at which hydrogen diffuses into a transition metal depends *inter alia* upon the surface condition of the metal. In an active condition penetration may occur freely, while in an inactive state, but under otherwise identical conditions, sorption may be almost completely inhibited. This behaviour draws attention to surface processes which may be much slower than interstitial diffusion. To some extent the nature of these processes is understood,[20] but a major problem has been to disentangle them from each other and from intracrystalline diffusion where all occur together. One approach to this problem is the "time-lag" method, in which gas is diffused through the metal in the form of a membrane. The steady state of flow is established only after an interval of time, and the final rate of flow expressed as a pressure-time curve approaches an asymptote which extrapolates to cut the axis of t and make an intercept L with it (Fig. 3).[21] In the absence of slow surface reactions, and when the membrane is initially free of gas, $L = \frac{l^2}{6D}$ where l is the membrane thickness (when in the form of a plate) and D is the diffusion coefficient.[22] If the membrane is a spherical shell of inner and outer radii a and b, $L = \frac{(b-a)^2}{6D}$; and if it is in the form of a hollow cylinder, $L = \frac{b^2 - a^2 + (b^2 + a^2)\ln a/b}{4D \ln a/b}$. These expressions become more complicated when slow phase-boundary reactions are also present.[23, 24]

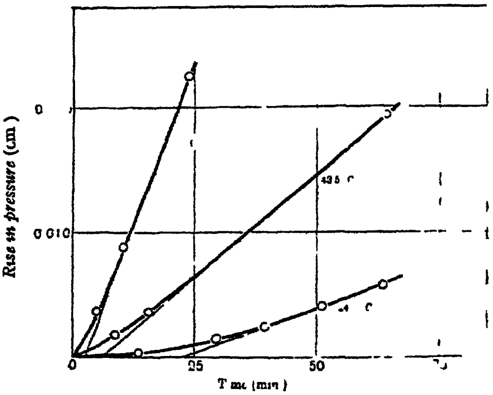

FIG 3—Time lags in establishing the steady state of flow of hydrogen through a hollow palladium cathode[21]

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[20] cf ref. 11, Ch. 4.

[21] Barrer, *Trans. Faraday Soc.*, 1940, **36**, 1235.

[22] Barrer, *Trans. Faraday Soc.*, 1939, **35**, 628.

[23] Barrer, *Phil. Mag.*, 1939 (7) **28**, 148

[24] Jaeger, *Trans. Faraday Soc.*, 1946, **42**, 615.

When D is determined using the simple expression $L = \frac{l^2}{6D}$ for a plate, and the steady-state permeation rate $-D\frac{\delta c}{\delta x} = D\frac{(C_o - C_l)}{l}$ is also measured, a value is obtained for $(C_o - C_l)$. If it is found that $(C_o - C_l)$ has the value it would possess when C_o and C_l are *equilibrium* concentrations (C_o and C_l being respectively the concentrations just inside the metal membrane at the faces, $x = 0$ and $x = l$), then it may be inferred that rate-controlling surface reactions are absent, or unimportant. If $C_o - C_l$ is smaller than corresponds to equilibrium, as is often the case, then surface reactions are comparable with diffusion,[23] and to eliminate these one must activate the surfaces, for example, by alternate oxidation and reduction, until equilibrium values of C_o and C_l are reached.

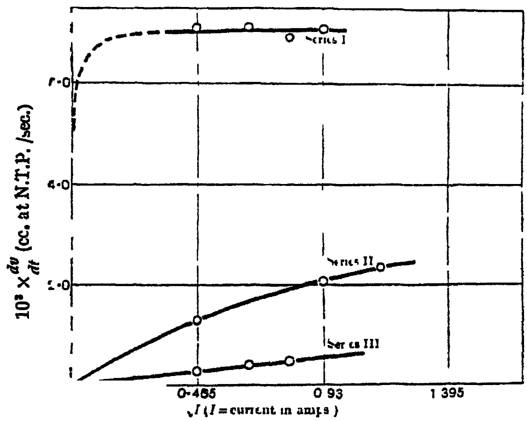

FIG. 4.—Influence of current density upon permeation velocity of H_2 through Pd in various stages of surface activity.[21]

In a study of diffusion of nascent hydrogen * in Pd and Fe using these methods,[21] progressive changes in the relative importance of surface reactions and of intracrystalline diffusion were followed. For a hollow Pd tube acting as cathode, calculated values of $C_o - C_l$ initially corresponded to saturation of the metal at $x = 0$, and $C_l < C_o$ at $x = l$. The surface activity of the metal steadily decreased however until $(C_o - C_l)$ was quite small, and surface reactions were rate-controlling.

A parallel phenomenon was also observed. At high current density and with the Pd surface in its most active state, the permeation rates were independent of current density, corresponding again to saturation for C_o and a small value for C_l. As $C_o - C_l$ decreased to parallel the decrease in activity of the Pd surface, the permeation rates P began to depend on the current density I while getting smaller in magnitude. At first, in an intermediate state of activity of the Pd, curves of P against $\sqrt{I}$ were convex away from the $\sqrt{I}$ axis. Finally, in the least active states of the Pd tube, the P against $\sqrt{I}$ curves were linear (Fig. 4).

(5) Rate-Controlling Phase-boundary Processes

Among the possible rate-controlling phase-boundary processes one may include the following:[25]

(i) an adsorbed atom enters the crystal lattice,

$$\text{Rate} = k_1\theta_1\left(1 - \frac{N_i}{N_s}\right) \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where θ_1 is the fraction of the surface covered by adsorbed atoms, N_i and N_s

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[25] Ref. 11, p. 178 *et seq.* Also Barrer, *Phil. Mag.*, 1939, (7) 28, 353.

* Generated, for example, at the metal surfaces by electrolysis.

have the same significance as previously (eqn. (7) and (8)) and k_1 is a rate constant;

(ii) a dissolved atom re-enters the surface,

$$\text{Rate} = k_2 N_t (1 - \theta_1) ; \quad . \quad . \quad . \quad . \quad (13)$$

(iii) a molecule strikes the surface and is adsorbed as atoms,

$$\text{Rate} = k_3 p_{H_2} (1 - \theta_1)^2 \quad . \quad . \quad . \quad . \quad (14)$$

where p_{H_2} denotes the hydrogen pressure;

(iv) two adsorbed atoms evaporate as a molecule,

$$\text{Rate} = k_4 \theta_1^2 ; \quad . \quad . \quad . \quad . \quad . \quad (15)$$

(v) a molecule strikes the surface, one atom being adsorbed and the other dissolved,

$$\text{Rate} = k_5 p_{H_2} (1 - \theta_1) \left(1 - \frac{N_t}{N_s}\right) ; \quad . \quad . \quad . \quad (16)$$

(vi) a dissolved atom combines with an adsorbed atom and evaporates as a molecule,

$$\text{Rate} = k_6 \,.\, N_t \,.\, \theta_1 \quad . \quad . \quad . \quad . \quad (17)$$

Barrer [23] first completely defined the steady-state permeation velocity in terms of all six of the above processes, and of the intracrystalline diffusion occurring simultaneously. Earlier treatments by Smithells and Ransley [26] and by Wang [27] are inadequate as they do not correctly formulate processes (i) and (v). It was also shown [23] that the concentrations of dissolved gas at the interfaces will, when phase-boundary processes are rate-controlling, be very different from their equilibrium values, and the concentration gradient $\frac{C_0 - C_l}{l}$ across the membrane becomes correspondingly very small. That is, the concentrations C_0 and C_l just within the ingoing and outgoing surfaces of the membrane respectively tend to become equal, C_0 being less than its equilibrium value and C_l greater than this value (cp. Section 4).

Moreover, it may well happen as a result of slow surface processes that even for pressures of 100 atm. or more on the ingoing side of the membrane, $C_0 - C_l$ may remain quite small, and so may the individual values of C_0 and C_l. Then the permeation rate may remain proportional to $p^{1/2}$ even when at high pressures. This explanation has been offered for the results of Smithells and Ransley on the high pressure permeation velocity of hydrogen through nickel.[25]

(6) Concentration Dependence of the Interstitial Diffusion Coefficient

The chance that the necessary sorption site adjacent to a given interstitial atom is vacant, so that a unit diffusion process may occur, is $\left(1 - \frac{N_t}{N_s}\right) = 1 - \theta$. Thus, in an ideal interstitial solution [28]

$$D = D_1(1 - \theta) \quad . \quad . \quad . \quad . \quad . \quad (18)$$

For a hydrogen "alloy" to which eqn. (6) applies, the above expression becomes

$$D = \frac{D_1}{1 + K_1\sqrt{p_{H_2}K_2}} \quad . \quad . \quad . \quad . \quad (19)$$

This concentration dependence of D means that the equation $\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$

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[26] Smithells and Ransley, *Proc. Roy. Soc. A*, 1936, **157**, 292.
[27] Wang, *Proc. Camb. Phil. Soc.*, 1936, **32**, 657.
[28] Barrer, *Trans. Faraday Soc.*, 1941, **37**, 590.

for diffusion in the metal must be replaced by $\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\frac{(D\partial c)}{\partial x}$. A combined study of steady-state flow and of sorption isotherm data may give both D_1 and the concentration dependence of D for any kind of diffusion system.[29] * Measurements of interstitial flow of gases in metals which treat this aspect of diffusion are lacking. However in an analogous study of diffusion in a zeolite,[31] D was shown to decrease in direct proportion as the interstitial concentration of the sorbate increased (cp. eqn. (18)), over a range of concentration values.†

Data of Wells and Mehl [32] for the diffusion of carbon in γ-iron do not conform to the foregoing model for an ideal interstitial diffusion. They found

$$D = D_0 \exp\left(\frac{-32{,}000}{RT}\right) \text{cm.}^2\text{sec.}^{-1}$$

with

$$D_0 = 0{\cdot}07\,(1 + 0{\cdot}87 \times \%\text{C}).$$

It is seen that D *increases* with increasing carbon content. However, departure from the simple theory is not surprising because the radius ratio C/Fe is about 0·6, on the limit for the formation of interstitial solutions. Two phases occur: carbon in cubic close-packed γ-iron (austenite), and carbon in body-centred cubic α-iron (ferrite). The limits of solubility are soon exceeded and then carbides such as cementite separate. Moreover in martensite, a supersaturated interstitial solid solution of carbon in α-iron, the cubic cell of the parent metal is deformed to a tetragonal one. Thus the system is complex and the interstitial structures are non-ideal in the sense that the parent lattice cannot readily accommodate the interstitial atom, and becomes increasingly distorted as the carbon content rises.

(7) Diffusion in the Presence of Impurity Elements

Many metals contain, in finished or intermediate states, traces of additional elements. These may have profound effects upon physical and chemical properties of the metal, including the diffusion of other elements within the metal. Little systematic study has been made of the influence of impurities on diffusion although some of the available information has been discussed.[33] Intra-metallic diffusion of an element may be accelerated or retarded by impurity: nitriding of iron occurs more rapidly when small amounts of oxygen are contained in the iron; nitriding the surface of steel in its turn accelerates the diffusion of hydrogen into the metal. On the other hand, increasing the carbon content of iron greatly decreases the rate at which sulphur penetrates the metal. Carbon retards also the rate at which phosphorus diffuses into iron.

The above more complex processes are only in part examples of interstitial diffusion. They may also typify diffusion in multi-component systems which, although of obvious importance, has not yet received much attention either in theory or experiment. In a three-component system involving elements A, B and C, diffusion of B may occur from the phase (A + B) to the phase (A + B + C) if the ***chemical potential*** of B in the three component phase is less than that in the two component one, even if the *concentration* of B is less in (A + B + C) than in (A + B). That is, diffusion may occur up as well as down a concentration gradient.[30] Thus the gradient in chemical potential, $\frac{\partial \mu}{\partial x}$, rather than the concentration gradient, $\frac{\partial c}{\partial x}$, provides the driving force in diffusion. The diffusion equation then becomes

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[29] Barrer, *Proc. Physic. Soc.*, 1946, **58**, 321.

[30] See e.g., Barrer, *J. Soc. Dyers Col.* (Symposium on Fibrous Proteins, 1946), p. 108.

[31] Barrer and Riley, *J. Chem. Soc.*, 1948, 133.

[32] *Trans. Amer. Inst. Min. Met. Eng.*, 1940, Tech. Publ. No. 1180.

[33] Ref. 11, p. 234 *et seq.*

* In the transient state of flow, a graphical procedure is also available for determining these properties.[30]

† In the zeolite, slow surface reactions do not interfere with free diffusion.

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(Dc\frac{\partial \mu}{\partial x}\right) \quad . \quad . \quad . \quad . \quad . \quad (20)$$

because the force on *each* particle is proportional to $\frac{\partial \mu}{\partial x}$, and so on all the particles to $c\frac{\partial \mu}{\partial x}$. The additional relationship $\partial \mu = RT\partial \ln a$, where a denotes the activity, then gives

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left[\frac{DcRT}{a} \cdot \frac{\partial a}{\partial x}\right] = \frac{\partial}{\partial x}\left[D_1\frac{\partial a}{\partial x}\right] \quad . \quad . \quad . \quad (21)$$

A recent investigation has been made of diffusion of copper both up and down concentration gradients in the ternary alloy Cu_4FeNi_3.[34] The alloy disproportionates below 800° c. to give two phases in which the relative proportions of iron to nickel remain unchanged but the proportions of copper alter, to give layers of each phase alternatively. Despite difficulties of interpretation some progress was made, and a general empirical equation advanced to describe diffusion either up or down gradients of concentration :

$$\partial \frac{(c_e - c)}{\partial t} = D\frac{\partial^2 (c_e - c)}{\partial x^2} \quad . \quad . \quad . \quad . \quad . \quad (22)$$

where c_e denotes the equilibrium concentration. This expression is compatible with eqn. (21) on making $(c_e - c) \propto a$, and $D \propto D_1$ but further assuming D independent of x or a. The alloy corresponds of course to a substitutive rather than an interstitial solution.

Summary

Some equilibrium and kinetic aspects of interstitial solid solutions have been examined. Conditions for forming such phases have been discussed, and a possible interpretation of the hardness and inertness of certain of these phases has been given in terms of a theory of the metallic bond due to Pauling. In many of these phases the number of contacts made by a metal atom rises above 12 to 16, 18 or 20, and all such contacts must be regarded as potentially bond-forming. Electrons forming these bonds resonate among the atoms forming them, inertness being associated in part with resonance energy, and hardness with the high co-ordination number. The change from paramagnetic pure metal to non-paramagnetic interstitial solution (e.g., $Pd\,H_{0 \cdot 6}$) follows from the theory.

Interstitial sorption equilibrium between gases and metals has been briefly reviewed, with particular reference to hydrogen " alloys." The entropy of occlusion may be a useful guide as to the mobility of the interstitial atoms, although the spacing of the entropy levels corresponding to different degrees of translational freedom of the occluded atom or molecule is less than previously considered.

Diffusion into metallic interstices may be governed *in tempo* by slow surface reactions, the nature of which is indicated. The diffusion coefficient D is, in any case, dependent upon the interstitial concentration of sorbate, so that the usual equation for transient flow must be generalised to $\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\frac{(D\partial c)}{\partial x}$. The occurrence of diffusion both up and down concentration gradients involves a further generalisation to $\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\frac{(D\partial a)}{\partial x}$ (a = activity).

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[34] Daniel, *Proc. Roy. Soc. A*, 1948, **192**, 575.

KINETICS OF NITROGEN EVOLUTION FROM AN IRON-NITROGEN INTERSTITIAL ALLOY

By Sir Charles Goodeve and K. H. Jack

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During recent years an intimate knowledge has been gained of the detailed mechanism by which reactions proceed in gases and solutions. Studies of reactions inside the solid phase or on its surface have not met with such success, largely because it has not been possible to isolate a single reaction from a number of consecutive ones, or because the product of the reaction has introduced the complication of a new phase. In the course of work by one of us (K.H.J.) to elucidate the structures of the iron nitrides, a particularly simple reaction has been found—the evolution of nitrogen from ε-iron nitride. The simplicity of this reaction arises from the fact that there is no substantial change in the structure of the solid phase accompanying the loss of nitrogen over the range studied.

The iron-atom arrangement of the ε-phase of the iron-nitrogen system (see Fig. 1) is close-packed hexagonal with the nitrogen atoms occupying certain of the octahedral interstices in an ordered manner. The phase has a relatively wide range of homogeneity from 35·5 N atoms to 49·3 N atoms per 100 Fe atoms at 400° C., i.e., approximately from Fe_3N to Fe_2N.* On thermal decomposition *in vacuo* or in an inert atmosphere the interstitial atoms are eliminated as molecular nitrogen, and in the temperature region, 350–500° C., studied in the present investigation a lower nitride, the face-centred cubic γ'-phase ("Fe_4N," 24·1–25·8 N atoms/100 Fe atoms) is formed. The γ'-phase decomposes above 400° C. giving the body-centred cubic α-phase containing about 0·4 N atoms/100 Fe atoms. The ζ-phase (49·5 to 50·8 N atoms/100 Fe atoms) is not included in either of the accepted phase diagrams [1] [2] but its existence has recently been confirmed.[3] The iron atoms in ζ- retain their same relative positions as in the ε-phase and are therefore in approximately close-packed hexagonal array, but, due to a rearrangement of the nitrogen atoms, the iron-atom lattice is anisotropically distorted. The same type of interstice is occupied in both ε and ζ so that the difference between the phases may be regarded as a second-order one and can be ignored for present purposes.

Elimination of nitrogen atoms within the limits of the ζ- and ε-phases (50·8 to 35·5 N atoms/100 Fe atoms) is accompanied by a gradual reduction of the unit-cell dimensions, the total of which, however, is only about 2 %, and since the relative positions of the iron atoms remain unaltered, this evolution of nitrogen is an example of the general reaction

$$\text{solid} \rightarrow \text{solid} + \text{gas} \qquad . \quad . \quad . \quad . \qquad (1)$$

in which one of the complicating factors, the solid-phase change, is absent.

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[1] Eisenhut and Kaupp, *Z. Elektrochem.*, 1930, **36**, 392.
[2] Lehrer, *Z. Elektrochem*, 1930, **36**, 383, 460.
[3] Jack, *Proc. Roy. Soc. A* (in press).

* Compositions of interstitial alloys are expressed in this paper as the number of interstitial atoms per 100 metal atoms rather than by weight or atomic per cent. or by stoichiometric formulæ.

The decomposition involves the successive processes:

(i) lattice diffusion of interstitial nitrogen atoms to " exposed " positions at the solid-gas interface,

(ii) combination of nitrogen atoms at the solid surface to give adsorbed nitrogen molecules,

(iii) desorption of nitrogen molecules.

The velocity of the reaction as a whole is determined by the velocity of the slowest of these three processes.

When ε- or ζ-iron nitrides are heated at temperatures below 500° C. in carbon monoxide, it has already been shown[3] that almost three-quarters of the original nitrogen atoms are gradually and isomorphously replaced by carbon atoms with only minor dimensional changes in crystal structure. The nitrogen is evolved mainly as nitrogen molecules and partly (not more than 25 %) as cyanogen. This reaction enables the elimination of nitrogen from iron nitrides to be followed kinetically down to much lower nitrogen concentrations than in the ordinary thermal decomposition, again without any complicating solid-phase change.

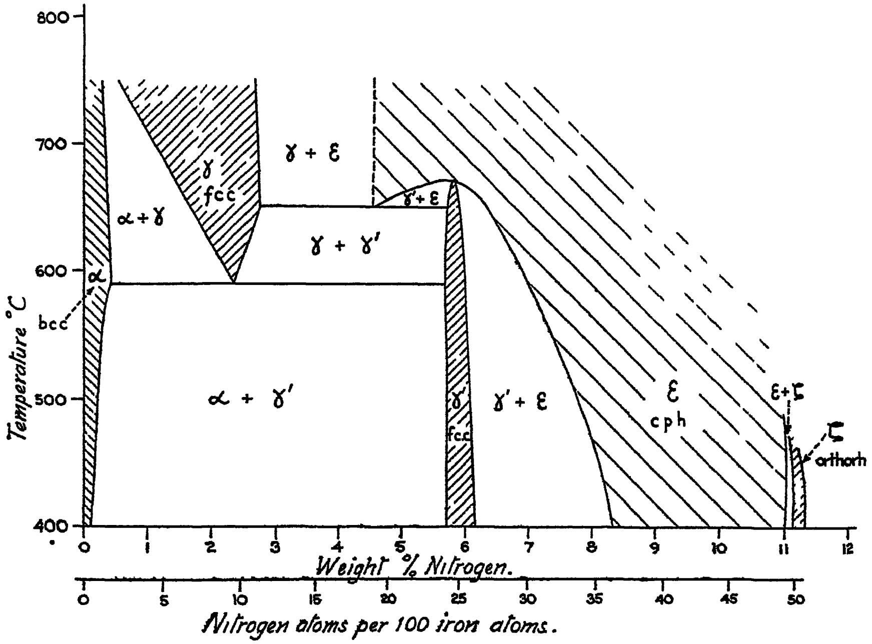

FIG 1 —Iron-nitrogen system

In a hydrogen atmosphere, nitrogen is eliminated from an iron nitride at temperatures from 250° C. to 450° C. entirely as ammonia.

By comparing the rates of denitriding of ε-iron nitrides *in vacuo*, in nitrogen, in carbon monoxide and in hydrogen, together with X-ray evidence, the nature of the rate-determining process in each of these reactions is deduced. Moreover, by applying simple calculations of the type already discussed by one of us,[4] the actual mechanism of denitriding is deduced.

Experimental

Homogeneous iron nitride powders (samples A, B, C, D, E, X, Y and Z) with nitrogen concentrations near the upper limit of the ε-phase were prepared by passing anhydrous ammonia over iron powder (99·9 % pure ; less than 300 mesh) at 400° c , 450° c. and 500° c. at such a rate that the partial pressure of hydrogen was negligible.[28] Microscopic examination showed that particles of nitride prepared in this way were approximately spherical with diameters closely grouped around 4 × 10^{-4} cm.

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[4] Goodeve, This Discussion.

In order to follow the thermal decomposition of the nitride, about 0·5g of sample contained in a silica boat was placed in the water-cooled end of the silica reaction tube, the centre portion of which was maintained within ± 2° c. of the required reaction temperature. The system was evacuated, and, after standing for at least 12 hr. to ensure absence of leaks, the boat and its contents were moved into the heated zone of the reaction tube by means of a magnetic device. Nitrogen pressures were observed at intervals on a mercury manometer and were assumed to be directly proportional to the amount of nitrogen evolved from the specimen. Decomposition was stopped at any desired stage by withdrawing the boat into the cooled end of the reaction tube. The total evolved nitrogen, calculated from Kjeldahl estimations of initial and final nitrides, was found to be equal to the loss in weight of the specimen.

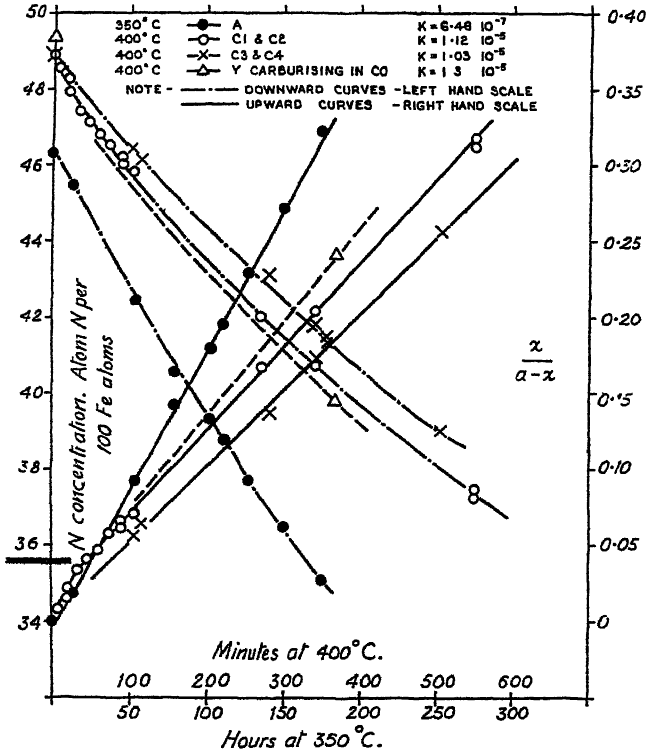

FIG. 2.—Decomposition of ε-Iron nitride at 350° c. and 400° c.

The rate of denitriding in hydrogen was followed by circulating pure hydrogen at 60 l./hr. over the nitride. The ammonia formed in the reaction

$$2N \text{ (interstitial)} + 3H_2 \rightarrow 2NH_3 \quad . \quad . \quad . \quad (2)$$

was condensed in liquid oxygen-cooled traps inserted in the system and hydrogen was continuously added from a gas burette to maintain the pressure at its initial value. As shown in Table II, the evolved nitrogen, again obtained from analytical results and loss in weight of the specimen, was found to be equal to that calculated according to eqn. (2) from the volume of hydrogen reacted. The nitrogen must therefore be evolved entirely as ammonia and thus the rate of addition of hydrogen was proportional to the rate of denitriding. The apparatus used for determining the rate of replacement of nitrogen by carbon in iron nitrides was similar to that used for denitriding in hydrogen. Details of the method are given elsewhere.[3] X-ray powder photographs were taken with crystal monochromatised Fe $K\alpha$ radiation in a 9 cm. Bradley camera.

Results

The broken curves of Fig. 2 and 3 correspond with the left-hand scale and show representative results for the decomposition *in vacuo* at 350° c., 400° c., 450° c. and 500° c. of ε-iron nitride powder specimens A, B, C, D and E, all with initial nitrogen concentrations near the upper limit of the phase By

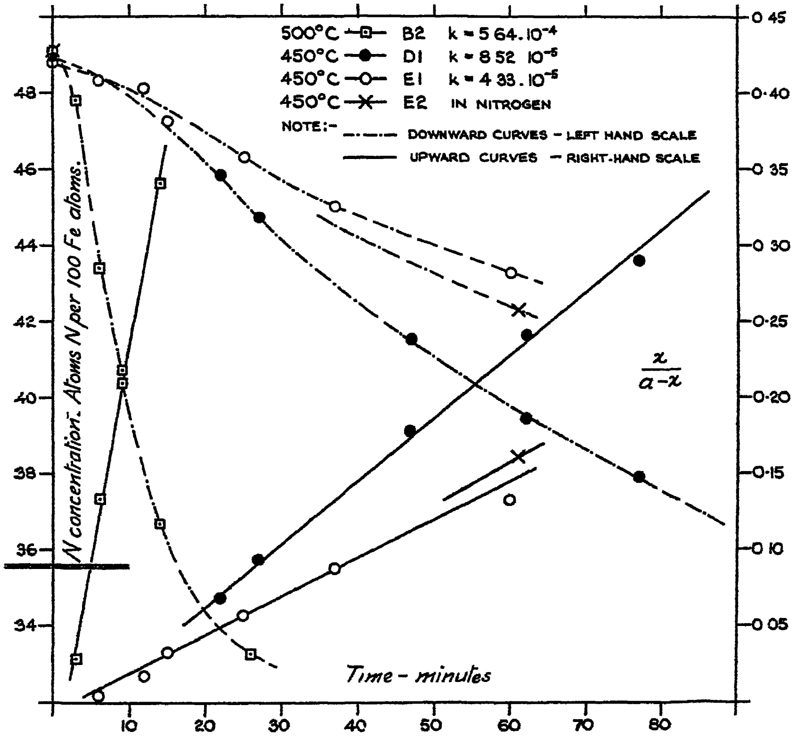

FIG. 3.—Decomposition of ε-iron nitride at 450° c. and 500° c.

" decomposition *in vacuo* " it is meant that evolution of nitrogen begins *in vacuo* but that, as the reaction proceeds, a pressure of molecular nitrogen builds up which in the experiments described was about 20 mm. Hg at the lower limit of the ε-phase. This lower phase limit is indicated in Fig. 2 and 3 by a double bar. The full curves, corresponding with the right-hand scale, show that within experimental error there is a linear relationship between $\frac{x}{(a-x)}$ and the time ; a is the initial interstitial nitrogen concentration and $(a-x)$ the concentration after a time t. Because of the relatively small variation in interstitial nitrogen concentration, it is insufficient to conclude from this observation alone that the rate of denitriding is given by a second-order kinetic equation. However, by comparing run Y with runs C1, C2, C3 and C4 (see Fig. 2) and also run Z with run D1 (see Fig. 4), it is clear that the rates of denitriding *in vacuo* at 400° c. and 450° c. are the same as the rates of elimination of nitrogen at these temperatures from iron nitrides carburised in carbon monoxide. It has already been shown[8] from different and more extensive experimental data that the rate of replacement of nitrogen by carbon is given by a kinetic equation of the second order with respect to the interstitial nitrogen concentration. The rate of denitriding *in vacuo* is also the same as that in an atmosphere of molecular nitrogen at 764 mm. Hg pressure.

Summarising, it is seen that the denitriding of ε-iron nitride proceeds at the same rate *in vacuo*, in nitrogen, and in carbon monoxide, so that the rate-controlling process is probably the same in each case.

Although there is fair agreement between separate experiments in which the same starting material is used (e.g , C1, C2, C3 and C4 ; Fig. 2), there are appreciable differences in the rates of reaction at the same temperature for initial nitride specimens prepared under different conditions (e.g , D1 and E1 ; Fig. 3). This, perhaps is a preliminary indication that the condition of the solid surface is an important factor in the rate-determining process.

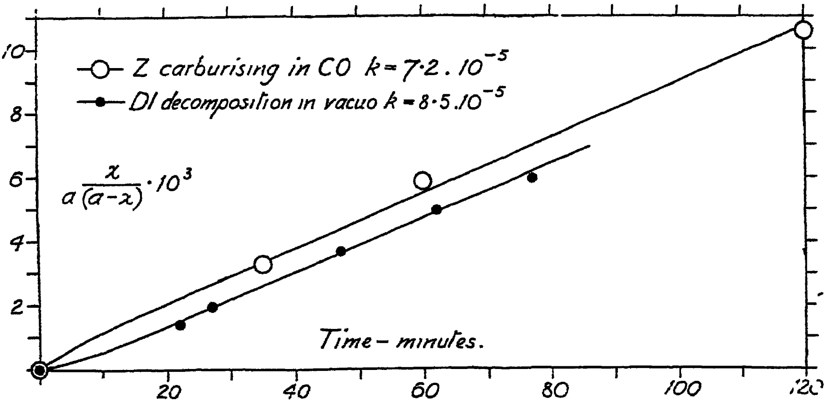

FIG. 4.—Evolution of nitrogen from ε-iron nitride at 450° C. by carburising with carbon monoxide and by decomposition *in vacuo*.

Table I summarises the results obtained for denitriding *in vacuo*, in nitrogen and in carbon monoxide ; *k*, the second-order velocity constant is given in units of (N atoms/100 Fe atoms)$^{-1}$ min.$^{-1}$.

TABLE I

DENITRIDING *in vacuo*, IN NITROGEN AND IN CARBON MONOXIDE

	In vacuo							In N_2	In CO			
Run . .	A	B1	C1 C2	C3 C4	D1	E1	B2	E2	Y	X1	X2	Z
Temperature ° C.	350	400	400	400	450	450	500	450	400	450	450	450
Gas pressure, mm. Hg	—	—	—	—	—	—	—	764	744	381	188	760
$k \times 10^7$	6·46	51·9	112	103	852	433	5640	536	130	340	363	720

Rates of denitriding in hydrogen were too rapid at 400° C. and 450° C. to be followed through their successive stages, but average rates of reaction within the limits of the ε-phase at 250° C., 300° C. and 350° C. are given in Table II. Without considering the order of this reaction it is clear that the rate of denitriding in hydrogen is about 10^4 times as rapid as denitriding *in vacuo*. In hydrogen, the gaseous reaction product is ammonia, the formation of which does not require the combination of two nitrogen atoms as in ordinary thermal decomposition. It seems probable, therefore, that the relative slowness of nitrogen elimination from the nitride *in vacuo*, or in molecular nitrogen, or in carbon monoxide, is a consequence of the slow rate of combination of pairs of nitrogen atoms at the solid surface. The movement of nitrogen atoms from the interior of the crystal lattice to the surface must be at least ten thousand times as fast during denitriding in hydrogen as during denitriding *in vacuo*. Thus, if we assume diffusion to be the rate-determining process in the former case it would be sufficiently rapid in the latter case for it *not* to be rate determining.

TABLE II

Denitriding in Hydrogen

Run		H1	H2	H3	H4	H5	H7	H8	H9	H10
Temperature, ° c.		450	400	300	250	350	300	350	350	250
Hydrogen pressure, mm. Hg		756	734	767	769	769	127	383	192	382
Initial rate of reaction (N atoms/100 Fe atoms) /min.		*	*	5·7	2·5	15·7	1·6	4·1	2·3	0·4
Weight loss, g. × 10^3		—	54	43	38	41	11	39	—	—
Weight of nitrogen evolved	(i) chemical analysis	65	54	43	38	41	9	39	48	23
	(ii) from volume of hydrogen reacted	66	53	43	36	40	9	38	47	21

* Reaction too rapid to be followed.

The X-ray photograph of the ε-nitride at each successive stage of decomposition *in vacuo* and in nitrogen shows a homogeneous solid phase with no appreciable line-broadening. The interstitial nitrogen concentration must therefore be almost constant throughout the iron-atom lattice. This absence of any marked concentration gradient again indicates that atomic diffusion is much more rapid than the slowest rate-determining process. From photographs published elsewhere [3] the same conclusion is reached in the replacement of nitrogen by carbon.

The rate of decomposition *in vacuo* increases rapidly with increasing temperature, and as shown by Fig. 5, the plot of log k against $1/T$ is approximately linear. Using the method of least squares to obtain the most probable value for the gradient of the graph, application of the Arrhenius equation gives a value of 42,100 ± 1400 cal. for the experimental activation energy, E.

Discussion

It is clear that the rate-determining process, with which is associated a high energy of activation, is the same *in vacuo*, in molecular nitrogen and in carbon monoxide, but is not the diffusion of nitrogen atoms from inside the crystal to the solid-gas interface.

Even in hydrogen, where denitriding occurs about 10^4 times as rapidly as in thermal decomposition, the diffusion process is not the sole rate-determining factor since variations in the hydrogen pressure have a marked effect upon the reaction rate.

Denitriding *in vacuo*; the Mechanism of the Surface Reaction.—If it is assumed that the rate-determining process in the thermal decomposition of ε-iron nitride at 350°–500° c. is the combination of nitrogen atoms at the solid surface,

$$2\,\mathrm{N}\ (\text{interstitial}) \rightarrow \mathrm{N}_2, \quad . \quad . \quad . \quad . \quad (3)$$

then the experimental observation that the reaction is of the second order with respect to the interstitial nitrogen concentration is explained. It follows that, in making this assumption, we identify the experimental activation energy E with the process given by eqn. (3). In view of our knowledge of the crystal structure of the solid phase it appears worth while to go farther than this and to attempt to picture the actual mechanism of the reaction.

If a model of a crystal of ε-iron nitride at its upper limit of homogeneity is broken in various ways, it is found that one nitrogen atom should be on, or freely accessible to, the surface for about every four iron atoms; i.e., there is one nitrogen atom for every 26 A.^{2} of surface area. These atoms will oscillate in their depressions or holes and will jump from one hole to another when they receive enough energy. They do this relatively freely inside the crystal lattice and therefore it is reasonable to assume that they will do so even more freely on the surface. However, since there is a strong tendency for nitrogen atoms in iron nitrides to keep as far apart as possible, we know that there is a repulsive force between them which is turned into an attractive force only at distances close enough to form the triple bond of the nitrogen molecule, N_2. In other words, there is an energy barrier opposing an attempt of one nitrogen atom to jump into a hole already occupied by another nitrogen atom. The distance between a pair of nitrogen atoms must be reduced from about 5 A. to about 1·5 A. before their mutual repulsion changes to a mutual attraction. During the approach of two nitrogen atoms, the energy barrier which must be surmounted should be substantial, but not as

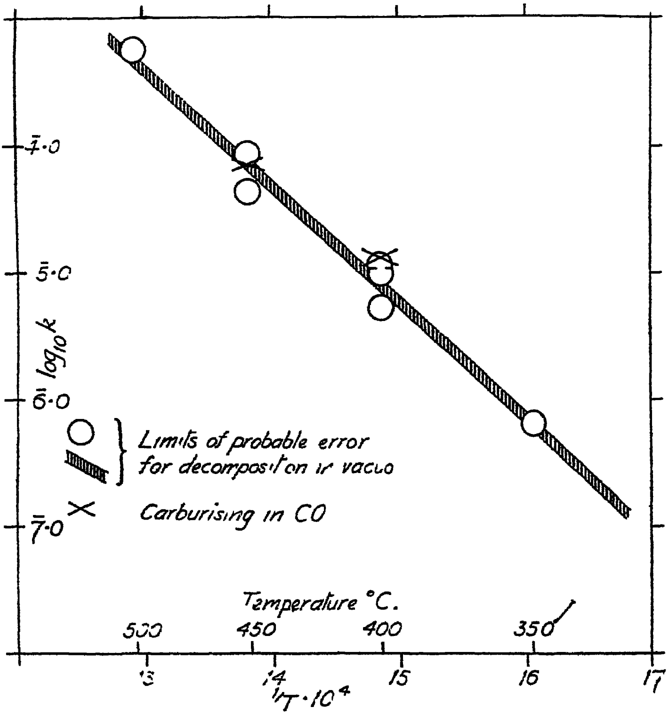

FIG. 5 —Variation with temperature of velocity constant k for the evolution of nitrogen from ε-iron nitride.

prohibitively high as it presumably is inside the crystal. It may be possible at some future date to estimate the height of this energy barrier from the forces required to remove the two atoms far enough from the surface of the iron and close enough together to form the N_2 molecule. At all events the identification of an activation energy of 42,100 cal./g. mol. with the process given by eqn. (3) is not incompatible with our existing knowledge of these forces. It seems reasonable to assume that the peak of the energy barrier lies at a N–N distance of 1·5 A., i.e., about 50 % more than the N–N distance in N_2.

The major assumption which it is proposed to make is that the number of attempts that a particular nitrogen atom makes to surmount this barrier (i.e., the number of collisions, Z_1) can be calculated by assuming that it travels about the surface with its average thermal velocity, $\bar{c} = \sqrt{\frac{8RT}{\pi M}}$. The justification of this assumption lies in the hypothesis that, while its net rate of travel is reduced by the fact that it performs a number of oscillations in each hole before it moves on, when it reaches a hole adjacent to the barrier these same oscillations amount to a compensating increase in the number of attempts to surmount the barrier while it remains in that hole. The same assumption has been made in applying, with considerable success, the laws of collision frequency in gases to reactions in solution.[5]

If, as in ordinary gas kinetics theory, we give all the diameter to the moving atom and consider the others as points, then this atom will sweep out in one second an area equal to $\bar{c}$ times the width of the energy barrier, w. In doing this it will collide with $\bar{c}wn$ atoms of nitrogen, where n is the number of atoms per cm.^{2} of surface. If N is the total number of nitrogen atoms on the surface of the nitride particle, the total number of collisions is $\frac{N\bar{c}wn}{2}$. As $e^{\frac{-E}{RT}}$ of these are successful, then the rate is

$$Z = \frac{N\bar{c}wn}{2} \cdot e^{\frac{-E}{RT}} \text{ molecules } N_2 \text{ per particle per second.}$$

The rate of evolution of nitrogen *atoms* per 100 iron atoms per second is thus

$$r = 2Z \cdot \frac{10^2}{A}$$

$$= \frac{N\bar{c}wn \cdot 10^2}{A} \cdot e^{\frac{-E}{RT}}$$

where A is the number of iron atoms in the nitride particle.

The appropriate value to take for w may be open to question, but it seems reasonable to take it at the peak of the barrier as we are only interested in those collisions which are successful, i.e., $w = 3$A.

From the known structure of ε-nitride at its upper homogeneity limit, and from the observed particle diameter, N, n and A are known. At 450° C.,

$$\begin{aligned} \bar{c} &= 1{\cdot}05 \times 10^5 \text{ cm./sec.} \\ N &= 1{\cdot}9 \times 10^8 \\ n &= 3{\cdot}8 \times 10^{14} \\ A &= 2{\cdot}3 \times 10^{12}. \end{aligned}$$

Thus, $r_{450^\circ \text{C.}} = (0{\cdot}7 \text{ to } 4{\cdot}3) \times 10^{-3}$ with a most probable value of $1{\cdot}8 \times 10^{-3}$ N atoms/100 Fe atoms/sec.

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[5] Hinshelwood, *The Kinetics of Chemical Change* (Oxford, 1942), p. 17

The observed initial rates of reaction at 450° C., given by the graphs of runs D1 and E1 (Fig. 3) and also calculated from the velocity constants, are :

D1 ; $3{\cdot}4 \times 10^{-3}$ (N atoms/100 Fe atoms) /sec.
E1 ; $1{\cdot}7 \times 10^{-3}$ (N atoms/100 Fe atoms) /sec.

Similar agreements are, of course, obtained at the other temperatures.

The agreement must be considered as largely coincidental in view of the assumptions made, but, in this kind of calculation, agreement within a factor 10 is considered significant and any other reasonable values of the quantities involved will not bring the agreement outside this range.

It might be argued that the rate-determining process could be the desorption of nitrogen from an activated adsorbed complex to the gaseous state. Suitable choice of equilibrium constants in the adsorbed layer might provide equally good agreement between theory and experiment. However, such a mechanism would require the existence of an adsorbed complex held to the crystal lattice by 42,100 cal./g. mol., i.e., something between van der Waals' forces and the binding forces between the iron and nitrogen atoms. The complexity of such a mechanism and the quantitative agreement of the simple recombination mechanism argue against a desorption theory.

Denitriding in Nitrogen and in Carbon Monoxide.—The absolute reaction rates for denitriding in nitrogen and in carbon monoxide are the same, within experimental error, as those for denitriding *in vacuo* so that the reaction mechanisms are very probably the same.

Dissociation pressures of iron nitrides are of the order of 4×10^4 atm. so that the system is far from thermodynamic equilibrium. It is not surprising then that variations from 0 to 760 mm. Hg in the pressure of molecular nitrogen have no effect upon the reaction rate.

In carburising ε-iron nitrides, reducing the pressure of carbon monoxide from 760 to 188 mm. Hg has no great effect upon the reaction rate. Again this fact is explicable if the rate-determining process is the combination of pairs of nitrogen atoms at the solid surface. In addition to the formation of N_2 molecules, however, an almost constant proportion (25 %) of the eliminated nitrogen appears to be evolved at 450° C. as cyanogen. The constancy of the 3/1 ratio of formation of nitrogen and cyanogen suggests that they are products of simultaneous side reactions.

Denitriding in Hydrogen.—Engelhardt and Wagner [6] concluded that in the reaction

$$\text{N (dissolved in } \alpha\text{-iron)} + \frac{3}{2}\,\text{H}_2\text{ (gas)} \rightarrow \text{NH}_3\text{ (gas)} \quad . \quad . \quad (4)$$

the rate was given by

$$-\frac{d[\text{N}]}{dt} \propto p_{\text{H}_2} \,.\, [\text{N}]$$

and that the rate-determining process was not the diffusion of nitrogen to the surface, but was the reaction,

$$\text{N (dissolved in } \alpha\text{-Fe)} + \text{H}_2 \rightarrow \text{NH}_2\text{ (adsorbed)} \quad . \quad . \quad (5)$$

occurring at the iron-gas interface.

In denitriding ε-iron nitride with hydrogen the results given in Table II show that the initial reaction rate varies with the hydrogen pressure but does not appear to be directly proportional to it. The experimental activation energy, calculated from the initial reaction rates of runs H3, H4 and H5 at 300°, 250° and 350° C. respectively, is about 12,000 cal. If it is assumed that NH_2 is formed by direct collision of hydrogen molecules from the gas phase with nitrogen atoms on the surface, then, using the above value for the activation energy of this supposed rate-determining process, the calculated reaction rate is about 10^8 times the observed velocity.

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[6] Engelhardt and Wagner, *Z. physik. Chem. B*, 1932, **18**, 369.

Alternatively, if it is assumed that the reaction occurs in the stages

(i) N (at the solid surface) + H (adsorbed) → NH (adsorbed) . (6)

(ii) NH (adsorbed) + H_2 (gas) → NH_3 . . . . . . (7)

with the former as rate determining, then the fraction of the surface covered by adsorbed hydrogen atoms must be not more than 10^{-6} in order to obtain reasonable agreement between observed and calculated rates of reaction.

X-ray evidence, however, indicates that the diffusion process in denitriding with hydrogen is rate determining to some extent. A photograph of the product H10 (11·5 N atoms/100 Fe atoms) showed the presence of ε-, γ'- and α-phases which cannot co-exist in equilibrium at any temperature. The concentration gradient in the α-phase is much smaller than in γ'- or ε-, so that we might expect diffusion processes to be rate determining towards the final stages of reaction, if not in the earlier stages. The rates of phase changes at these low temperatures may be equally important.

It must be concluded that the reaction of hydrogen with iron nitrides is apparently too complex for its absolute velocity to be predicted from any simple rate-determining mechanism.

The authors wish to thank Prof. Sir Lawrence Bragg for providing facilities for one of us (K.H.J.) at the Cavendish Laboratory, Cambridge.

Summary

The rate of nitrogen evolution from ε-iron nitride at 350°–500° c. is given by a kinetic equation of the second order with respect to the interstitial nitrogen concentration and is associated with an activation energy of 42,100 ± 1400 cal./g. mol. The velocity of diffusion of the nitrogen atoms to the surface is at least 10^4 times as rapid as the rate-determining process. The rate-controlling stage of the reaction is considered to be the combination of pairs of nitrogen atoms at the solid surface. By calculating the collision frequency on the assumption that this surface reaction behaves as in a two-dimensional gas, the correct order of magnitude for the absolute reaction rate is predicted.

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NOTES ON THE EXPERIMENTAL TECHNIQUE OF SOME PHYSICO-CHEMICAL MEASUREMENTS BETWEEN 1000° AND 2000° C.

By J. A. Kitchener and J. O'M. Bockris

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Although information exists in the literature regarding the special materials, apparatus and methods of research of use at temperatures above 1000° c., it has been the experience of the present authors in undertaking work in this field that an extensive search and enquiry is needed to decide on a reliable experimental technique suitable for a given problem. The restrictions imposed by the refractory materials form the chief obstacles to the study of the physical chemistry of phenomena at high temperatures. The production, control and measurement of the temperature also present special problems in some cases, because not all of the varied methods reported in the literature are of value to the physical chemist.

It seems therefore that a critical review of the scope and limitations of some of the techniques which have been found suitable for physico-chemical work at temperatures in the range of 1000° c. to 2000° c. might be useful to other workers entering the field. The following notes are based partly on original observations and techniques and partly on information collected from various sources which have been tested by, and proved of value to, the present authors.

Since high temperature work is closely dependent on the refractories available, it should be pointed out that these notes apply particularly to methods which are practicable in Britain at present. The scope of high temperature research may extend considerably when better refractories become readily available and in this connection it appears that research on the so-called super-refractories (e.g., boron nitride) is urgently needed.

I. Furnaces

(i) Furnaces for Physico-chemical Research in the Temperature Range 1000°–2000° c. Temperatures up to 2000° c. may be produced in several ways, few of which are suitable for physico-chemical measurements. For this purpose, it is generally necessary to have (*a*) a uniform temperature zone, (*b*) a controlled atmosphere and (*c*) means of regulating and reproducing the temperature to within narrow limits. Consequently, although serviceable in certain cases, gas heating[1] (with or without oxygen), carbon tube or spiral,[2] or carbon granule electric furnaces,[3] carborundum rod heaters,[4] or electric arcs[5] are not generally useful as they fall short of the three general requirements in one way or another.

The most versatile and useful methods of heating are by means of high frequency induction or by resistance wires or strips. High frequency heating is the most suitable method where a moderate mass of metal is to be melted or where a crucible of graphite or metal can be used, since the refractory problem is reduced to a minimum, only the substance under examination and its container being raised to the highest temperature. The temperature can also be controlled readily, and, in the case of molten metals, the stirring caused by eddy currents aids attainment of uniform conditions. High frequency heating has been used successfully, for example, in cases where the rapid quenching following interruption of the high frequency current was desirable.[6] Unfortunately, the auxiliary apparatus required to generate high frequency currents with sufficient power is large and expensive although oscillators which can be made in the laboratory have been described.[7]

Heating by resistance wires fulfils all the requirements suggested above and is within the means of most laboratories. Nichrome, which is commonly used for lower temperatures owing to its low temperature coefficient of resistance, is not serviceable above 1100° c.; pure nickel (m.p. 1450° c.) is available for use in the absence of oxygen. Resistance furnaces wound with platinum are extensively used for temperatures up to about 1500° c. The m.p. of pure platinum is 1750° c. but platinum furnaces may not be used at temperatures much higher than 1500° c. owing to the rapid evaporation of platinum, which becomes serious at 1600° c. The high cost is the chief disadvantage in this case, as it is, *a fortiori*, with rhodium (m.p. 1960° c.) which would otherwise have considerable potentialities as a resistance wire.

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[1] e.g., Outhard, *Gas World*, **122**, No. 3155.

[2] Arsem, *Amer. Electrochem. Soc. Trans.*, 1906, **9**, 153. Atkins, Kramers, Pirani and Weil, *Coal Res.*, Dec., 1946, Appendix 1.

[3] Pirani, *Coal Res.*, 1944, 61.

[4] e.g., Heyroth, *U.S. Pat.* 2,319,323, 1943.

[5] Balajiva, Quarrel and Vajragupta, *J. Iron Steel Inst.* (Advance Copy, 1946); (No. 34/1946 of the Ingot Comm.).

[6] Chipman and Ta Li, *Trans. Amer. Inst. Met.*, 1937, **25**, 425.

[7] Aitchison, *J. Sci. Instr.*, 1948, **25**, 136.

The most useful resistance wire is molybdenum (m.p. 2620° c.). Tungsten is more refractory (m.p. 3200° c) and is, therefore, to be preferred for temperatures above 2000° c. but it is less easily wound on refractory tubes. Both these metals suffer from the disadvantage that they must be used in a reducing atmosphere. However, this involves little difficulty in furnace design and the cheapness and availability of molybdenum makes it preferable to platinum even for the lower temperature range, the molybdenum furnace being limited at the upper temperature range chiefly by the properties of the refractory tube on which the heating element is wound.

(ii) Advantages and Practical Aspects of Molybdenum Resistance Furnaces. Advantage attaching to molybdenum resistance furnaces over other types of electric furnaces can be summarised as follows:

1. No characteristic shape or size of the hot zone is necessary. Several different refractory materials are inert to molybdenum in appropriate atmospheres even at very high temperatures (e.g., zirconia, beryllia, alumina, mullite).
2. Molybdenum furnaces are comparatively easily constructed.
3. A uniform temperature zone is relatively easily obtained, e.g., by winding the tube more closely at the ends than in the middle. For a uniformity of temperature of ±5° c. at 1650° c. over a length of 2", the ratio of length to diameter of the furnace must be about 10/1 for a uniformly wound wire.[8]
4. Temperatures in excess of 2000° c. can be reached with molybdenum windings.
5. Molybdenum furnace windings in a controlled atmosphere have a particularly long life : they are seldom the limiting factor in the life of a furnace tube.
6. The temperature control is easier than with other types of furnaces. Control is particularly rapid in the case of the open grid type of winding described later where the temperature changes in the crucible chamber follow almost immediately upon alteration in transformer voltage. As there is negligible deterioration of the molybdenum or tungsten, temperature-current characteristics remain approximately constant, which facilitates the initial adjustment of the power necessary to produce a given temperature.

Simple molybdenum furnaces can be made easily in the laboratory and one type thus made is described elsewhere in this Discussion.[9] The molybdenum is wound, preferably in strip * form, on a refractory tube. The use of strip is preferable to that of wire as it gives a greater heating surface area for a given cross-section and can be wound more uniformly. The strip may be secured at the ends by another turn of molybdenum wire, treble leads being used to connect the windings to the terminals, and the winding is then coated with a cement consisting of pure alumina powder mixed with some organic binder. The purpose of the cement is to insulate the turns and to give protection against mechanical shock, the wires becoming brittle after long periods at high temperature. For the latter reason, also, thick wire is preferable to thin. It has the further advantage that a low voltage with high current is then used, thus reducing the danger of short circuits, although conversely use of a very high current incurs difficulties of electrical supply. The tube is insulated by a considerable thickness of calcined alumina powder.

The atmospheres used with molybdenum resistance furnaces may be pure hydrogen, "forming gas" (nitrogen-hydrogen mixtures), or cracked ammonia (made by passing dry ammonia gas through a furnace packed with steel wool and heated to 850° c.). The "running-in" of a new furnace tube should be carried out with extreme caution, the temperature being raised very gradually from ordinary to maximum temperatures, e.g., for a 3" Al_2O_3 tube, not less than 3–4 days is advisable as the initial running-in period. It is said to be desirable to hold the temperature of such a tube in the range of 1300°–1400° c. for 12–24 hr. before exceeding the latter temperature.

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[8] Mr. C. R. Barber, private communication.

[9] Kitchener, Bockris and Liberman, This Discussion.

* For wires, the optimum thickness is 0·9–1·4 mm. This is connected with the present method of manufacture which makes it difficult to get long ductile wires without brittle spots above this thickness.

During the heating period the current is kept approximately constant, the voltage being advanced gradually, as the resistance of molybdenum increases greatly with temperature. This is conveniently achieved by use of a continuously variable auto-transformer. The temperature coefficient of the resistance of molybdenum is an advantage in the sense that it tends to make the furnace self-compensating for fluctuations in the mains voltage, and in practice temperatures constant to approximately ±5° c. at 1500°–1700° c. are obtained with a well-lagged furnace which is not subjected to irregular ambient temperatures. Auxiliary thermo-regulators are sometimes also used and these are based upon thermocouples, resistance thermometers, or the resistance of the furnace windings themselves.

Even after the first running-in, the heating should still be slow and it would be inadvisable to take furnaces (such as those described below) from room temperatures to 1800° c. in less than about 5–12 hr. The shorter time reduces the life of the refractory tube which is particularly liable to crack at the ends owing to the large temperature gradient between the end of the winding and that of the tube. In many types of molybdenum furnace, a cracked tube can be satisfactorily repaired repeatedly with the appropriate cement.

Moisture is always present in the furnace when cold: to reduce the water content considerably may be very desirable. Thus, at high temperatures, water may attack molybdenum and, in the absence of hydrogen (e.g., in an argon atmosphere), produce molybdenum oxides which attack the refractory tube. Water may also attack graphite crucibles and under normal conditions it thus appears difficult to use graphite crucibles inside the furnace in a hydrogen atmosphere without their suffering serious attack unless water is rigorously excluded. The complete elimination of water vapour from furnaces is usually very difficult; however, the water content is considerably reduced by maintaining the furnace tube initially for some hours at about 1000° c.

(iii) Furnaces for Electrical Measurements up to 2000° c.

(*a*) Requirements. Extensive work on the conductivity of molten substances has been recorded in the literature only with substances in the temperature range below 800° c.; [10] [11] [12] few systematic measurements are recorded in the range 800°–1000° c.; [13] [14] no measurements have previously been recorded above 1600° c. (but see this Discussion [15]).

The chief requirements in design of apparatus for such work are to overcome the following difficulties:

(1) distortion of containing vessels and electrodes,

(2) pollution of liquids by contact with refractory materials either by dissolution or by reaction,

(3) non-uniformity of temperature in the vessel containing the melt,

(4) electrolytic polarisation, and

(5) lack of reliable thermocouples in consequence of which optical pyrometers are used. Some substances fume, however, when the temperature is greater than about 1500° c., thus making simple optical measurements unsatisfactory.

In recent preliminary work on the measurement of the electrical properties of silicate melts at Imperial College the following methods were used in conductivity measurements to avoid these difficulties. The pollution of the molten liquid was successfully avoided by the use of molybdenum for crucibles and electrodes. A compromise between the requirements of a uniform temperature and of a comparatively large distance apart of the electrodes (so that the resistance to be measured does not become too small) was met by having a crucible of 2" diam. with electrodes about 1" apart. The difficulty of optical pyrometer measurements was overcome by use of a molybdenum sighting sheath as described below.

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[10] Summary of earlier works: Biltz and Klemm, *Z. anorg. Chem.*, 1926, **152**, 267.

[11] Biltz and Klemm, *Z. anorg. Chem.*, 1924, **110**, 318.

[12] Rishkevich, *Z. Elektrochem.*, 1937, **39**, 531.

[13] Arndt and Kalass, *Z. Elektrochem.*, 1924, **30**, 12.

[14] Jaeger and Kapma, *Z. anorg. Chem.*, 1920, **113**, 27.

[15] Bockris, Kitchener, Ignatowicz and Tomlinson, This Discussion.

Electrolytic polarisation is considerably decreased by the increase in temperature and higher frequency of the A C in a Wheatstone network. In a typical binary silicate the variation of conductivity with frequency in a typical lime-silica mixture (65 % CaO) at 1650° was <1 % over the range 500–10,000 c./sec. The molybdenum electrodes were at a fixed distance apart and could be moved vertically by means of the lifting gear shown in Fig 1. The position of the electrodes was known to within 0·1 mm [*] Two types of furnaces have been used in these measurements and the essential features of these are outlined below.

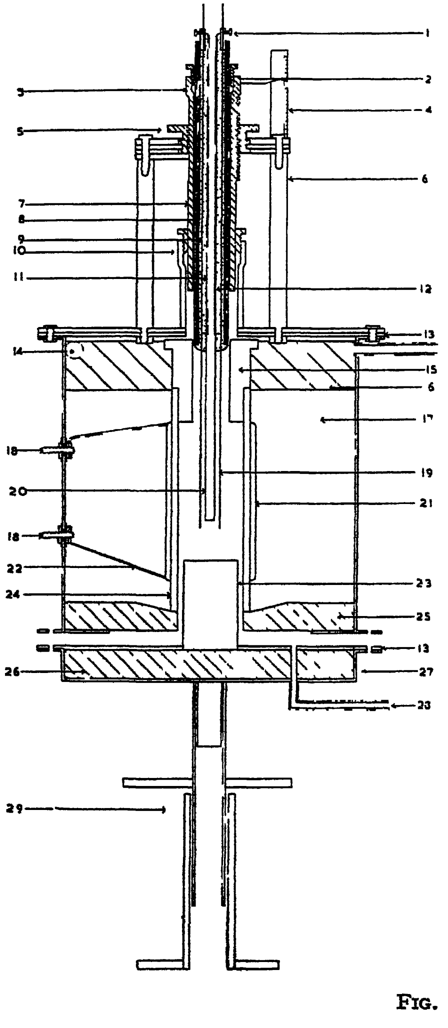

DIAGRAM OF CONSTRUCTION OF TUBE-TYPE MOLYBDENUM FURNACE.

1. Electrode clamp.
2. Pointer.
3. Gas-tight gland, asbestos packed
4. Centimetre scale.
5. Gear for raising and lowering electrodes.
6. Support for lifting gear.
7. Brass tube.
8. 2" alumina tube.
9. 0·2 cm. molybdenum electrodes.
10. Gas-tight gland asbestos packed.
11. ½" alumina tube.
12. Alumina cement.
13. Uralite sheet.
14. Hydrogen inlet tube.
15. Alumina cement plug.
16. HT1 brick.
17. Calcined alumina powder.
18. Terminals.
19. Molybdenum electrodes.
20. Sighting tube (molybdenum).
21. Winding (details not shown).
22. Tails of winding.
23. Alumina cement pedestal.
24. 4" alumina tube.
25. Firecrete cement base to furnace
26. Firecrete cement.
27. Removable bottom of furnace.
28. Hydrogen outlet.
29. Gear for raising and lowering furnace bottom.

FIG. 1.

(*b*) TUBE TYPE OF FURNACE. This was essentially a molybdenum-wound resistance furnace with a recrystallised alumina tube of 3" to 4" internal diam. (see Fig. 1 and Plate 3).[†] Behaviour of this type of furnace was satisfactory in an atmosphere of dry hydrogen or "forming gas." In some experiments, argon was used and this was dried and nitrogen removed by passage over activated calcium at 400° C., but even after this purification, parts of the inside of the furnace were found to be blackened and attacked if a complete experiment were carried out in an argon atmosphere. This attack is thought to be due to water vapour as it was found to be reduced by heating for a preliminary period of some 12 hr. in pure dry hydrogen at about 1000° C. As a standard procedure in experiments carried out in the presence of an argon atmosphere, heating up to, and cooling down from, 1000° C. is carried out in hydrogen and no noticeable attack on the molybdenum occurs.

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[*] For further details of conductivity measurements made with this arrangement, see elsewhere in this Discussion.[15]

[†] Two models of this furnace were made differing essentially only in the diameter of the main tube, the larger furnace being intended for experiments on electrolysis

Thermal Characteristics: In normal practice, temperatures in the region of 1800° C could be obtained in about 6 hr. from a commencement at ordinary temperature and by maintaining a constant current of about 60 amp. About 4–5 kw. are necessary to maintain the furnace at the temperatures 1700°–1800° C. Cooling was allowed to take place freely for about 12 hr., the temperature reaching about 200° C. in this time.

Durability of Refractories: The quality of the various recrystallised alumina tubes, though nominally the same, appears to vary. Usually, when the furnace was put through its cycle of heat changes about 3 times per week, the life of the tube was about 3–4 months. It is probable that effective agents in accelerating the breakdown of refractories are SiO and SiO_2 in the vapour state derived from silicate melts under examination. A black deposit, also visible in the tube and possibly due to oxidation products of Mo, appeared to be sometimes connected with tube failures.

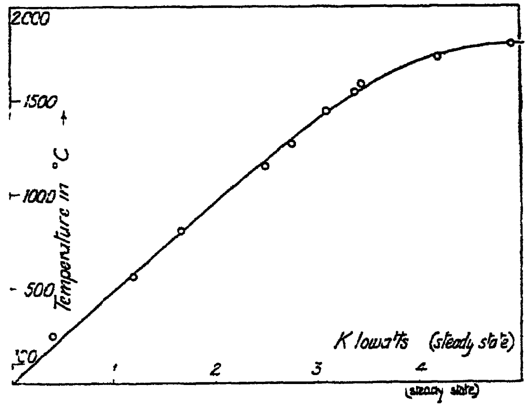
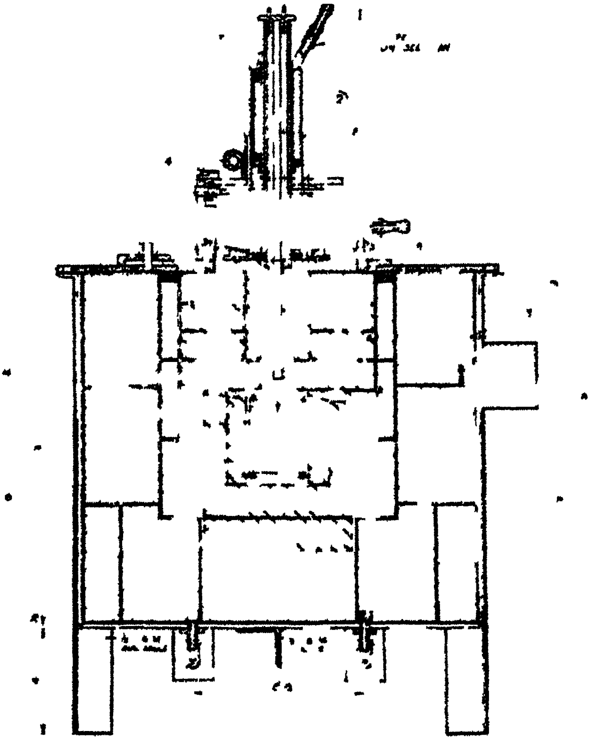


FIG. 3.—Power-temperature relation for grid type furnace.

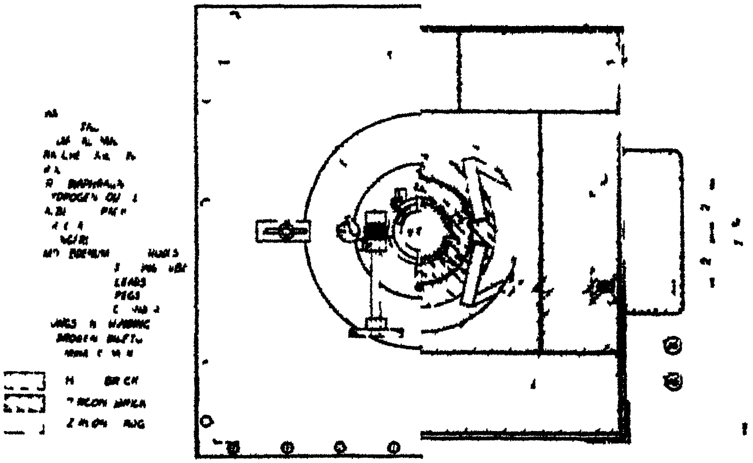
(*c*) GRID WINDING TYPE OF FURNACE. A furnace somewhat different in detail to the tube type was also constructed and used. The principal differences are as follows: The refractory used was a micronised zircon brick. As shown in Fig 2 and Plate 1, this was arranged in the form of a central cylindrical cavity in place of the usual alumina tube. The use of this type of zircon enables a higher temperature, namely, 2000° C., to be attained, than the use of alumina. Conversely, the thermal conductivity of zircon is greater than that of alumina so that extensive insulation in the form of high temperature insulating bricks (which will withstand a temperature of 1400° C.) has to be employed.

The heating element consisted of tungsten wire which was substituted for molybdenum in this furnace on account of its higher melting point. The winding was arranged in an open grid form, as shown in Fig. 2 and Plate 2. The cylindrical sheet of molybdenum visible in the photograph had the object of increasing the temperature uniformity in the crucible chamber. It is necessary to suspend the tungsten winding by hooks of *molybdenum* attached to the zircon, owing to the reaction of tungsten with zircon. This type of winding appears advantageous because the direct heating without a refractory tube facilitates rapid temperature changes in the crucible chamber.

The lifting gear was somewhat different in detail from that of the tube-type furnace (see Plate 2). An improvement is the iris-diaphragm clutch for compressing the asbestos packing around the alumina tube, thus making a practically gas-tight fit between tube and furnace case when the tube is fixed in an appropriate position. The power-temperature relation from this furnace is shown in Fig. 3.



GENERAL ARRANGEMENT



HALF SECTIONAL PLAN ON A A

ELECTRIC FURNACE
GRID TYPE WINDING

FIG 2.

To face page 96

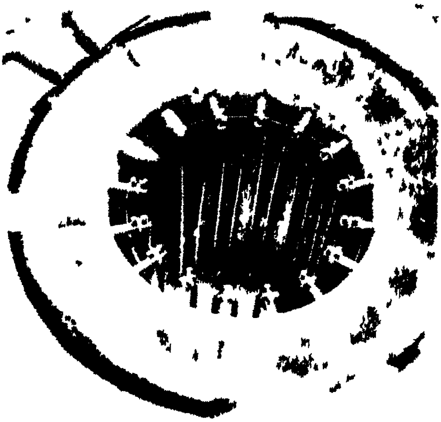


PLATE 1

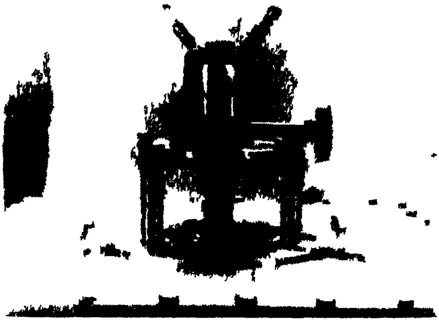


PLATE 2.

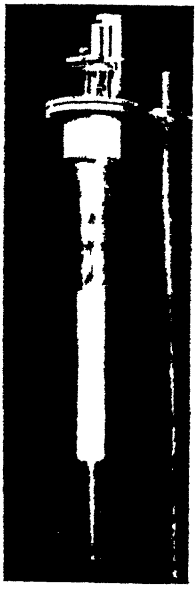


PLATE 3

II. Temperature Measurement

(i) Accuracy and Limitation of Thermocouples. The standard instruments for temperature measurement in the range 1000° to 2000° c. are thermocouples and optical pyrometers.[16] Platinum resistance thermometers are rarely used above 1000° c. Total radiation pyrometers should be applicable in cases where there is a large aperture at uniform temperature on which the pyrometer could be sighted. Novel inventions such as the tin-in-graphite thermometer[17] seem to have met with little favour.

The type of thermocouple most usually employed for the range 800°–1500° c. is that of pure platinum against a 13 % rhodium-platinum alloy (see [16]). These couples are now commercially available in highly standardised materials, and the makers guarantee their reliability without further calibration to within ±1° up to 1100°, ±2° for 1100°–1400°, and ±3° for 1400°–1600°. There are very few researches in which the reproducibility attainable on the other measurements involved demands more accurate temperature limits than these and, in any case, it is a matter of great difficulty to attain higher (absolute) precision.

Even the limits of temperature measurements quoted can only be obtained by careful avoidance of various sources of error. The chief of these are contamination and evaporation. It has been shown[18] that contamination is frequently associated with volatilisation of silica which takes place when any siliceous materials are heated to temperatures above 900° under reducing conditions. Contact of the couple with sulphur and carbon must also be avoided. Whenever possible, therefore, thermocouples should be used in an impervious sheath of alumina which should also be open to the air.[19] Under these conditions, contamination errors are negligible. It is a simple matter to check a couple from time to time against a new one and, in case of error, to cut off about an inch of the wires to make a new junction.

Errors ascribed to change of composition are said to arise through preferential volatilisation of rhodium.[19] This clearly increases with increase of temperature and length of exposure, and for this reason 1400° c. is generally given as the highest temperature at which platinum couples can be used continuously for long periods (in the absence of contamination). For the measurement of higher temperatures the quick immersion technique may be adopted, the wires being normally kept withdrawn in a region at about 1400° c. inside the sheath and pushed along to the end of the sheath when readings are to be taken. Temperatures up to 1700° c. may be measured in this way to ±5° c.

Other thermocouples have sometimes been suggested for higher temperatures. The graphite-carborundum couple of Fitterer[7] has not been used extensively in research, but several workers have used tungsten-molybdenum couples.[20] Views on the value of these couples are discrepant. It appears that although they give relatively constant readings over long periods (when electrically screened and protected from oxidation) they need to be frequently checked against platinum thermocouples or optical pyrometers when correct absolute temperature measurements are required. Their main use is in the maintenance of constant furnace temperatures.

(ii) Optical Pyrometry at Temperatures above 1600° c. A disappearing filament type of optical pyrometer was compared with the polarising type and the former was found to be superior to the latter with regard to accuracy of observation. With three different observers, consistence of measurement at about 1650° c. was about three times better with the disappearing filament than with the polarising type.

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[16] (*a*) Griffiths, *Methods of Measuring Temperature* (1947), 3rd Ed. (*b*) *Temperature, its measurement and control in Science and Industry* (American Institute of Physics, 1941).

[17] Northrup, *Pyrometry* (1920).

[18] Symposium on the Contamination of Platinum Thermocouples, *J. Iron Steel Inst.*, 1947, **155**, 213.

[19] Homewood, ref. 16 (*b*), p. 1272.

[20] Osan and Schroder, *Arch. Eisenmittenw.*, 1933, **7**, 89 ; Leiber. *ibid*, 1937-38, **2**, 63 ; Fornander and Omberg, *Jernkontorets Annalen*, 1939, **123**. 527.

In order to obtain the greatest accuracy with a disappearing filament pyrometer, it is necessary to pay attention to the following details.[21]

1. A flat filament should be used, this being superior to the cylindrical type of element. Care must also be taken to ascertain that the length/diameter ratio of the lamp filament is not too short owing to the possible introduction of temperature coefficient and thermal inertia errors in short filaments.

2. High magnification should be obtained by use of Huyghens eyepiece

3. The absorption screen should be in the form of a slide at right angles to the axis. This avoids the possibility that, if an absorption screen is interposed by rotation about an axis at right angles to the axis telescope, the screen may be tilted in the beam of radiation, unless the " in " position is very well defined, thus causing reduced transmission of light to the screen. Pyrometers were built with special attention to the above points and found very satisfactory for accurate laboratory work.

In measurements of the temperature of molten slags, no ordinary method of sighting the pyrometer on the slag surface could be used because of the fumes evolved from the slags at temperatures above about 1500° c. A tube of molybdenum (closed at the lower end) was cemented into a vertical alumina tube (see Plate 3) and the height of the molybdenum tube adjusted until it was just above the surface of the slag. The pyrometer was then sighted on the bottom of the molybdenum tube. The largest diameter of molybdenum tube used was ½″ and it was found by direct measurement that a length of about 2″ at the bottom of this tube was in a zone the temperature of which was constant to within about 10°. According to Buckley[22] for tungsten (emissivity 0·4) with diffusely reflecting walls and bottom, the radiation from a cylindrical hole is within 1 % of full if the ratio of length to radius is 8, as is the case in the apparatus reported here. A deficiency of 1 % in the total radiation gives rise to a negligible error in optical pyrometer measurements up to 2000° c.

By direct comparison between the optical pyrometer and an insulated Pt-Pt/Rh thermocouple placed at the bottom of the tube, agreement to within ±5° was obtained up to 1600° c. At higher temperatures, the agreement in the estimated reading of three independent observers was obtained to within about the same limits.

III. Laboratory Refractories : Use of Molybdenum.

(i) **Attackability.** Reliable observations concerning the attack of molten substances of definite composition, particularly slags, on refractories are difficult to find.[23] The most important characteristics of a refractory in this connection are low porosity and stability to temperature changes. These factors are affective in a way largely independent of chemical composition. The main requirement is that the eutectic temperature of the final products of the reaction between refractory and slag is higher than the working temperature. This condition is said to be best reached by refractories of magnesia-chromium sesquioxide-alumina.

A method sometimes applicable in reducing the attack of slags on refractories is to cool the refractory walls to some 50° c. below the temperature of the slag. For a modern review on laboratory refractories see Kirby.[24]

The problem of providing a satisfactory container when both slag and metal are present is a very difficult one, though frequent in metallurgical work. Some workers claim that a carbon lining is satisfactory in such cases.[30] A technique of more general applicability is that of the spinning crucible in which the metal forms a lining on the crucible wall by centrifugal action, thus reducing the resultant attack of the slag on the crucible[31] (see also Foëx[32] for remarks on the velocity of the slag-metal interaction).

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[21] Barber, *J. Iron Steel Inst.*, 1945, **152**, 171 P.

[22] Buckley, *Phil. Mag.*, 1936, **17**, 576.

[23] Endell, *Ber. dtsch. keram. Ges.*, 1938, **19**, 471.

[24] Kirby, *Metallurgia*, 1944, **30**, 65.

[30] Vosburgh, *Met. Alloys*, 1939, **10**, 133; Bleck and Mellor, *U.S. Pat.* 2,351,594.

[31] e.g., see Taylor and Chipman, *Amer. Inst. Min. Met. Eng.*, No. 1499, 1942 ; Barrett *et al.*, *Amer. Inst. Min. Met. Eng.*, 1939, **135**, 73; Northrup, *U.S. Pat.* 1,378,189.

[32] Foëx *et al.*, *Compt. rend.*, 1943, **216**, 268.

(ii) Use of Molybdenum. Pure molybdenum offers good possibilities for use as a crucible material to contain slags, etc Its chief advantage lies in its resistance to the attack of these systems and its high m p. The relevant physical and chemical properties of molybdenum are summarised in Table I.

The construction of a variety of objects of molybdenum, e.g , crucibles, tubes, U-tubes, etc., was achieved by a welding technique between molybdenum and carbon arcs. It is important that the carbon should be the cathode. The welding is carried out in an atmosphere of dry forming gas contained in an inverted bell jar about 4″ diam and 9″ deep. A rapid flow of gas must be maintained, or else oxidation of the molybdenum occurs and the weld is brittle. Thus in making crucibles, 0·2 mm. thick Mo is used. The cylindrical sides of the crucible are pressed in the cold around a suitably shaped former and the crucible bottom is pressed out of sheet molybdenum. These parts are then welded together under the conditions described above. It has recently been possible to draw small cups out of molybdenum which has been pretreated in a certain way.[29] This method does not appear to offer any notable advantages over the welding method. At the same time it is more expensive and of less general application.

TABLE I

PROPERTIES OF PURE MOLYBDENUM

Physical Properties	Chemical Properties
Hardness (Moh's scale) : 8·5	H_2 : does not absorb
Tensile strength : 0·125 mm. diam.	H_2O : reacts very slowly at room temperature ; at 700° c., reacts→oxide.
Coefft. of linear expansion : $=5{\cdot}56\times10^{-4}$	N_2 : reaction at 1000° c. (Zschukoff).[25] No reaction at 1200° (Moissan).[26] All N_2 absorbed at 0·3 mm. pressure at 2000°–2400° c. (Langmuir).[27]
Thermal conductivity at 1648° c : 1·0 w./cm./° c.	
M p. 2620° c. approx.	NH_3 : no reaction at red heat.
B.p. 4700° c. approx.	CO : no reaction at white heat.[28]
Log (rate of evaporation)$=17{\cdot}11-38{,}600\ T-1{\cdot}76\log T$ g./sq. cm./sec.	
Log v.p.$=17{\cdot}354-38{,}600\ T-1{\cdot}26\log T$	
Specific elect. resistance 41·2 micro ohms/cm.^{3} at 1648° c.	

The attack of most non-ferrous slags on molybdenum is negligibly small. Thus, an extreme test was carried out by heating and cooling slags of composition 35 % CaO and 65 % SiO_2 to 1800° c. four times for 2–3 hr. on each occasion. After this treatment analysis of the slag showed it to contain 0·06 % MoO_3. Molybdenum crucibles will not withstand the attack of "pure" FeO.

The authors' thanks are due to the following : Dr. M. Pirani for help in the general design of the grid type furnace and Mr. E. Forster of the B.C.U.R.A. for help in the practical design and construction of this furnace ; Dr. N. P. Allen and Dr. V. H. Stott of the Metallurgy Division, National

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[25] Zschukoff, *Ann. Inst. Anal. Physique Chim.*, 1926, **3**, 14.
[26] Moissan, *Compt. rend.*, 1935, **120**, 1230.
[27] Langmuir, *J. Amer. Chem. Soc.*, 1919, **41**, 167.
[28] Tomlinson (unpublished).
[29] Mr. J. H. E. Jeffes, private communication.

Physical Laboratory, for helpful discussions; Mr. C. R. Barber of the Physics Division, National Physical Laboratory, for advice in the design of some of the optical pyrometers used; Dr. J. H. Partridge of the G.E.C. for advice with regard to the welding of molybdenum; and Mr. James Royce of James Royce Furnaces Ltd. for extensive and friendly co-operation in the design and construction of the tube type electrical resistance furnaces.

The authors also wish to thank their colleagues, Dr. F. D. Richardson and Messrs. J. H. E. Jeffes, S. Ignatowicz and J. W. Tomlinson, for helpful discussions.

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ELIMINATION OF THE THERMAL-DIFFUSION ERROR IN STUDIES OF GAS-METAL EQUILIBRIUM

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Experimental studies of the compositions of gaseous mixtures in equilibrium with a metal and its oxide at high temperatures have been much used in determining the free energy of oxides. In a number of cases the results have been subject to error or uncertainty on account of the partial thermal separation of the gases in a temperature gradient. Emmett and Schultz[1] showed that all the early results of static determination of equilibria involving hydrogen and water vapour suffered from this source of error which was as great as 40 % in some reported H_2O/H_2 ratios. Eastman and Ruben[2] pointed out that even flowing systems are not immune. Shibata and Kitigawa[3] also studied the effect and applied corrections to their data on reduction equilibria. More recently Darken and Gurry[4] have measured the amount of thermal separation in gaseous mixtures flowing into, or out of, a vertical tube furnace and described conditions for avoiding error in this kind of system.

In equilibria involving oxygen in solution in a molten metal this source of error has been especially troublesome. The added difficulty arises from the necessity of working in a temperature gradient when high-melting point metals such as iron are being studied. The simplest method for stirring the melt and thus bringing its interior into equilibrium with the gas is to use high-frequency induction heating. For this reason the sample cannot be placed in the centre of a tube furnace where thermal separation would be a minimum. When a cold mixture of hydrogen and water vapour impinges upon the surface of such a melt, thermal diffusion opposes the approach of the heavier water molecule to the surface with the result that the surface layer of gas is enriched in hydrogen and the molten metal depleted in oxygen below the concentration which would be in equilibrium with gas of the inlet composition. It was shown by Chipman and Fontana [5] that this phenomenon led to errors of about 20 % in the equilibrium constant at 1600° C. and that the error could be at least partially eliminated by preheating the entrant gas mixture. The desire for greater accuracy in the equilibrium measurements has led to the present investigation of this source of error.

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[1] Emmett and Schultz, *J. Amer. Chem. Soc.*, 1933, **55**, 1376.
[2] Eastman and Ruben, *J. Amer. Chem. Soc.*, 1935, **57**, 97.
[3] Shibata and Kitigawa, *J. Chem. Soc., Japan*, 1935, **56**, 722 and 736.
[4] Darken and Gurry, *J. Amer. Chem. Soc.*, 1945, **67**, 1398.

Thermal Diffusion

The phenomenon of thermal diffusion in gases was predicted by Enskog [6] in 1911, and independently by Chapman[7] in 1916; it was observed for the first time by Chapman and Dootson[8] in 1917. In his work on the kinetic theory of gases, Chapman has shown mathematically that a temperature gradient in a mixture of two gases is in general sufficient to produce a partial separation. Chapman's theory is based upon considerations of intermolecular force-fields and upon the relative molecular weights, sizes and numerical concentrations affecting the separating tendencies in a mixture of two gases subjected to a temperature gradient. Later Ibbs [9] and others also verified it experimentally.

In order to arrive at a working formula Chapman has simplified his more general theory by assuming rigid, elastic and spherical molecules and by other approximations. The resulting approximate formula for a binary mixture is of the form

$$k_t = \frac{dx_1}{d\ln T} = \frac{Ax_1 + Bx_2}{1 + Cx_1/x_2 + Dx_2/x_1} \quad . \quad . \quad (1)$$

where x denotes the mole fraction, T the absolute temperature and the coefficients A to D are functions of the molecular weights and the ratios of the diameters.

Recently Gillespie [10] developed a simple theory of thermal diffusion based on elementary kinetic considerations. His treatment does not account for the dependence of the effect on the size of the molecules and their mutual forces, but is based solely on molecular weight which is the variable of major importance.

The equation for a binary mixture is obtained by equating the net bombardment of each species across a plane between two adjacent thin layers of the gas mixture to the amount of each species returned across the plane by a return flow. The average temperature of the layers differs by dT, and the bombardment of each species is assumed independent and calculable in any layer in the way the pressure of an ideal gas at constant temperature is calculated. Thus, for a binary mixture we have

$$\frac{d\ln x_1}{d\ln T} = \frac{x_2(m_2 - m_1)}{2(m_1x_1 + m_2x_2)} \quad . \quad . \quad . \quad (2)$$

where T denotes absolute temperature, x mole fraction and m the square root of the molecular weight.

Comparing the values of separation as calculated from (1) and (2) with those experimentally obtained by Elliot and Masson [11] for three mixtures of gases over practically the same temperature range (about 0° to 500° C.), Gillespie showed that his eqn. (2) gives considerably better results. In another comparison[10] involving nine different binary mixtures,[12 13] the mean difference in favour of eqn. (2) was 15 %.

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[5] Chipman and Fontana, *J. Amer. Chem. Soc.*, 1934, **56**, 2011.

[6] Enskog, *Physik Z.*, 1911, **12**, 56 and 533

[7] Chapman, *Phil. Trans. Roy Soc A.*, 1916, **216**, 279; 1917, **217**, 115.

[8] Chapman and Dootson, *Phil. Mag.*, 1917, **33**, 248.

[9] Ibbs *Physica*, 1937, **4**, 1133.

[10] Gillespie, *J. Chem. Physics*, 1939, **7**, 530.

[11] Elliot and Masson, *Proc. Roy. Soc. A*, 1925, **108**, 378.

Gillespie also showed that when there is any number q of species, comparing gas 1 with any gas i in which i runs over all values from 1 to q, we have

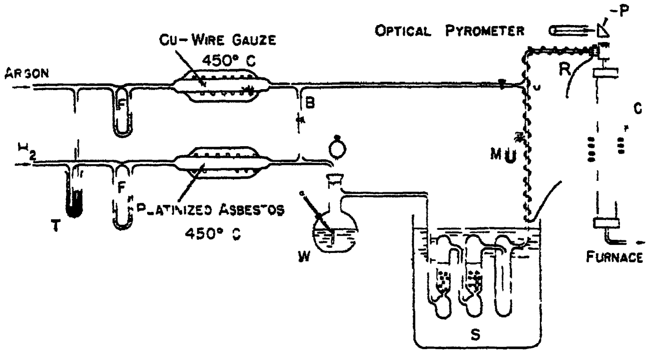
$$\frac{d \ln x_1}{d \ln T} = \frac{1 - m_1}{2 \sum m_i x_i} \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

where the summation is over all the species.

Eqn. (3) can be applied to find the theoretical effect of foreign gases on the separation of two gases of kinds 1 and 2. Writing an equation of the type of (3) for the second gas and subtracting from (3) we find

$$\frac{d \ln (x_1/x_2)}{d \ln T} = \frac{m_2 - m_1}{2 \sum m_i x_i} \quad . \quad . \quad . \quad . \qquad (4)$$

According to this equation the relative separation of two gases by thermal diffusion, defined as the left-hand side of eqn. (4), is inversely proportional to the mean root molecular weight of the mixture and it can therefore be decreased by addition of a third gas of high molecular weight.



T — Trap
F — Flowmeter
W — Water bath
S — Saturator
B — By-pass

M — Manometer
R — Chromel heater
P — Glass prism
C — Induction coil

FIG. 1 —Schematic diagram of apparatus used in equilibrium studies.

Experimental

The objective of the present study was to investigate the possible methods for eliminating the thermal diffusion error in the determination of equilibrium in the reaction of hydrogen and water vapour with molten iron containing dissolved oxygen. This reaction, which occupies a key position in the application of thermodynamics to reactions of steelmaking, has already been studied fairly extensively. As a result of earlier studies [14] it is known that the concentration of oxygen in the melt is proportional to the steam/hydrogen ratio, or that the activity of oxygen is proportional to its concentration. Hence the equation for the reaction and its equilibrium constant are written

$$\text{O (in liquid Fe)} + \text{H}_2(g) = \text{H}_2\text{O}(g) \; ; \; K = \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2} \times \% \text{O}} \quad . \qquad (5)$$

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[12] Ibbs and Wakeman, *Proc. Roy. Soc. A.*, 1932, **134**, 613.
[13] Ibbs, Grew and Hirst, *Proc. Physic. Soc.*, 1929, **41**, 456.
[14] Fontana and Chipman, *Trans. Amer. Soc. Met.*, 1936, **24**, 313.

The apparatus was designed to provide controlled preheating of the inlet gases and ready admixture of an inert gas in controlled amounts. A known mixture of water vapour and hydrogen was obtained by saturating purified hydrogen with water vapour at controlled temperature. This mixture, with or without addition of a purified inert gas, was passed over the surface of a small melt (approximately 70 g.) of electrolytic iron in a closed induction furnace. After sufficient time at constant temperature for attainment of equilibrium the melt was cooled and analysed for oxygen.

In any experiment in which thermal diffusion has occurred, the apparent value of K in eqn. (5) is larger than its true value. It was the purpose of this study to obtain values of the apparent K under a series of conditions which would permit an extrapolation, with the aid of eqn. (4), to obtain the true value of K.

Apparatus

GAS SYSTEM.—A schematic diagram of the apparatus is shown in Fig. 1. Commercial hydrogen obtained in the usual tank cylinder was passed through a needle valve and led to the safety trap (T) which, containing mercury, was used to relieve excess tank-side pressure. The flowmeter (F) was used to determine the amount of hydrogen gas passing through the system. The catalytic chamber (C) was used to convert any contaminated oxygen in the commercial hydrogen into water vapour with platinised asbestos. The temperature of the catalyst was kept at about 450° c. A by-pass (B) with stopcocks was provided so that the hydrogen could be introduced directly from the tank to the furnace when desired. From the catalytic chamber the gas passed through a water bath (W), kept at the desired temperature by an auxiliary heating unit, so that the gas was burdened with approximately the proper amount of water vapour before it was introduced into the saturator (S).

All connections beyond the catalytic chamber were of all-glass construction. Those connections beyond the water bath were heated to above 80° c. to prevent the condensation of water vapour by means of a chromel wire wound around the tubing and covered with asbestos. After the saturator a third gas (helium or argon) was led into the steam-hydrogen line at (J), and finally the ternary mixture was introduced into the furnace.

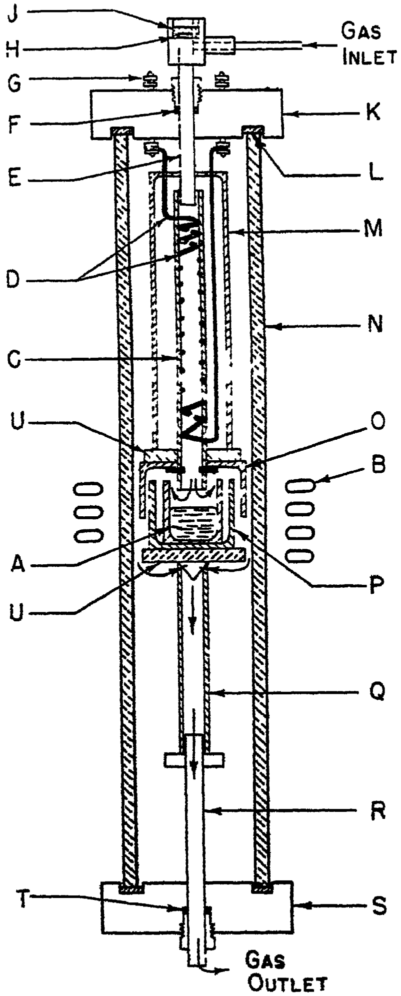
When argon was used as the foreign gas to prevent thermal diffusion it was first passed through the flowmeter (F) and then purified of the trace of free oxygen in it by passing it over heated copper wire gauze at 450° c. It was then led into the furnace along with the steam-hydrogen mixture. All connections after the purifying system were of all Pyrex-glass construction. A few heats were also made with helium as the third gas. It contained 0·3 % hydrogen as an impurity and had to be purified by passing the gas over CuO needles at 500° c. and thus converting the hydrogen to water vapour and absorbing it in a U-tube filled with phosphorus pentoxide.

Mercury-vapour runs presented a dual problem of generating and introducing the vapour into the furnace without contamination with the outside atmosphere. For this purpose a Pyrex flask fitted with a Glass-Col heater was used to generate the vapour. At the inlet end of the furnace the Pyrex tubing was sealed to a Covar tube which was silver-soldered onto the brass furnace top. Condensation of the mercury vapour within the tube or the furnace top was prevented by adequate resistance-heating of both to about 400° c. Due to the known hazards of working with mercury vapour, great care was exercised to catch all the vapour in condensed form at the bottom of the furnace, which had to be specially designed for this purpose. The weight of the liquid mercury thus collected over a definite time interval was used to compute the rate of flow of the vapour.

THE SATURATOR.—The saturator unit comprised three glass chambers, as shown in Fig. 1, with the first two chambers packed with glass beads and partially filled with water, and the third empty as the entrainment chamber. Each tower has a glass tube with a stopper attached for the purpose of adjusting the amount of water in it. This unit was immersed in a large oil bath, which was automatically controlled to constant temperature, ±0·05° c.

FURNACE ARRANGEMENT.—The furnace arrangement is shown in Fig. 2. A glazed-surface silica tube (N), 24 in. long and 2 in. inside diam., was used throughout. It worked satisfactorily and was impermeable to gases at elevated temperatures. The furnace was equipped with water-cooled brass top (K) and bottom (S). A rubber washer (L) helped to seal it off from the outside atmosphere. The brass head (K) was fitted with a sight glass (J) made of Pyrex glass, ½ in. diam. and 1/16 in. thick, to facilitate temperature measurements from the top by means of an optical pyrometer.

Gas inlet and outlet were provided at the top and bottom of the furnace respectively. A small silica tube, ½ in. outside diam. and 5 in. long, was used to carry the mixture into the furnace. It was fixed to the furnace head by means of an asbestos gasket (F). The preheater tube (C) was suspended from the small quartz tube.



A — Alumina crucible containing melt
B — Induction coil, 16 turns
C — Preheater tube (alundum)
D — Platinum-coil preheater
E — Quartz tube, ½ in. O.D.
F — Asbestos gasket
G — Terminal, preheater coil
H — Rubber gasket
J — Sight glass
K — Brass top (water-cooled)
L — Rubber ring
M — Insulating sleeve (alundum)
N — Glazed quartz tube, 24 in. long, 2 in. int. diam.
O — Insulating thimble (alundum)
P — Outer crucible (alundum)
Q — Supporting tube (alundum)
R — Stainless steel tube
S — Brass bottom (water-cooled)
T — Rubber gasket
U — Supporting discs (alundum)

FIG. 2.—Furnace arrangement

The alumina crucible (A) was placed inside an outer alundum thimble (P), resting on an alundum disc (U) which was in turn supported on top of an alundum tube (Q) ½ in. inside diam. and 5 in. long. The final support was a stainless steel tube (R), ½ in. inside diam., which was fixed to the bottom by means of a rubber gasket and which could be slid up or down as desired. This proved to be very effective in positioning the melt inside the induction coil to get the desired electrical coupling.

The furnace was completed with an induction coil 2½ in. diam., actuated by a Lepel unit of 7½ to 30 kw. input, which proved to be satisfactory. The power needed for melting was from 10 to 15 kw. and only 5 to 8 kw. were necessary to hold the metal at 1563° c.

THE PREHEATER.—The preheater tube (C) made of alundum, ½ in inside diam., was tapped with 12 threads to the inch for a length of 6 in.; a coil of platinum wire (D), 0·025 in. diam., which served as the heating element, was screwed into position in the threads. Later on, a bigger and better preheater was made 9 in. long and with a heavier wire, 0·030 in diam., using platinum-10 % rhodium instead of pure platinum. This enabled the entering gaseous mixture to be heated up to the temperature of the melt before coming in contact with it. The leads were taken out through holes drilled in the preheater tube and were fastened to terminal connectors at G. An independent source of power supply was used for resistance heating through a rheostat such that it could be regulated to get the desired amount of preheat. The preheater was covered with an alundum insulating sleeve (M), 12 in. long and 1½ in. diam., resting on an alundum disc (U) and another sleeve (O), 1½ in. long and 1¾ in. diam., to prevent excessive radiation. The incoming gases came in direct contact with the heated platinum wire and hence the preheating was very efficient.

CALIBRATION OF APPARATUS.—The flowmeters were calibrated by collecting and measuring the gas passing through in a measured time. The saturator was checked by absorbing and weighing the water vapour carried over by a measured volume of hydrogen which in several determinations agreed closely with the theoretical. The oxygen content of the purified gases was found to be negligibly small. Thermometers were calibrated against a standard platinum resistance thermometer. The optical pyrometer was checked frequently against the freezing point of electrolytic iron in hydrogen, which was taken as 1535° c. Readings were taken on the surface of the liquid metal and it was established in a parallel study that the emissivity of this surface did not vary measurably within the temperature range here considered (1535° c.–1563° c.).

Oxygen analyses were made by the vacuum-fusion method on an apparatus which has been in use in this laboratory over a period of 10 yr. It had been calibrated previously against measured gas volumes and checked by exchange of samples with the National Bureau of Standards. Results reported are the mean of two or more concordant determinations.

PROCEDURE.—A charge of about 70 g. electrolytic iron contained in an alumina crucible was melted in slightly moist hydrogen and brought to a temperature of 1563° c. It was held at this temperature by hand control of the power input. Frequent temperature measurements were made and in general these did not deviate more than ± 5° c. from the desired value. The saturator was controlled at 54·0° c. to give a nearly constant ratio of water vapour to hydrogen whose exact value was determined by the barometric pressure. Preliminary experiments had demonstrated that under these conditions a constant oxygen content was reached after 15 min. All runs were continued for a minimum of 45 min. after which the metal was chilled as rapidly as possible by lowering it into the cold part of the furnace.

The experimental conditions included the use of three levels of preheater temperature as well as a few runs without preheat. The temperature of the platinum coil was measured by means of an optical pyrometer and corrected for emissivity and absorption in the intervening optical system. The temperature of the heater at low, intermediate and high levels of preheat was estimated to be 800° c., 1200° c. and 1563° c. respectively during the runs.

Experiments were made without gas admixture and with addition of the inert gases helium, argon and mercury. Previous results had indicated that the rate of flow of the gases had a decided effect on the equilibrium constant The preheating of the gaseous mixture was more efficient the lower the linear velocity of the gas stream as it approached the hot metal surface. But it was found from a few preliminary runs that the rate of flow did not make any difference because of the better and more efficient gas preheater used in this work.

Results

The results of successful heats are summarised in Table I. The second column of the table gives the ratio of steam to hydrogen in the furnace as computed from the barometric pressure and the vapour pressure of water in the saturator,

TABLE I

EQUILIBRIUM DATA AT 1563° C.

Heat Number	$\left(\frac{P_{H_2O}}{P_{H_2}}\right)$ corrected	% Oxygen	Rate of Gas Flow ml /min.		*K* (Appar.)	Preheat Conditions
			H_2	Addition		
A. ARGON ADDITION						
1	0·1751	0·0338	245	380	5·17	Low (approx. 800° c.)
3	0·1740	0·0339	245	380	5·14	„
4	0·1741	0·0326	245	380	5·33	„
6	0·1748	0·0337	245	380	5·16	Intermediate (approx 1200° c)
7	0·1760	0·0316	700	150	5·57	Low
8	0·1759	0·0351	150	1000	5·03	„
9	0·1720	0·0321	150	150	5·36	„
11	0·1724	0·0279	150	0	6·17	„
12	0·1742	0·0344	150	150	5·08	Intermediate
13	0·1743	0·0349	150	1000	4·99	„
14	0·1743	0·0323	700	150	5·39	„
16	0·1742	0·0277	245	0	6·30	None
17	0·1741	0·0287	245	0	6·08	Low
18	0·1742	0·0283	245	0	6·15	Intermediate
19	0·1743	0·0315	150	1000	5·53	None
20	0·1743	0·0321	700	150	5·44	„
26	0·1732	0·0343	250	1000	5·04	Intermediate
27	0·1732	0·0357	250	1000	4·86	„
54	0·1731	0·0340	250	500	5·08	„
56	0·1732	0·0342	300	1000	5·06	„
79	0·1732	0·0352	250	0	4·91	High (approx. 1563° c.)
80	0·1732	0·0308	250	250	5·60	„
81	0·1732	0·0362	250	500	4·76	„
82	0·1732	0·0413	250	1000	4·19	„
91	0·1742	0·0386	250	0	4·53	„
92	0·1743	0·0387	250	250	4·52	„
93	0·1754	0·0362	250	500	4·83	„
94	0·1754	0·0396	250	1000	4·44	„
99	0·1743	0·0370	250	0	4·72	„
100	0·1738	0·0354	250	250	4·89	„
101	0·1738	0·0390	250	500	4·45	„
102	0·1728	0·0373	250	1000	4·63	„
B. HELIUM ADDITION						
28	0·1734	0·0308	250	250	5·63	Intermediate
29	0·1735	0·0296	250	250	5·79	„
31	0·1738	0·0303	250	250	5·72	„
32	0·1728	0·0305	250	500	5·65	„
33	0·1712	0·0306	250	1000	5·58	„
34	0·1740	0·0302	250	250	5·75	„
37	0·1725	0·0309	250	1000	5·57	„
C. Hg-VAPOUR ADDITION						
43	0·1736	0·0367	250	480	4·73	„
49	0·1735	0·0361	250	520	4·82	„
50	0·1735	0·0363	250	480	4·77	„
51	0·1735	0·0337	250	500	5·15	„
52	0·1736	0·0362	250	510	4·77	„
55	0·1732	0·0363	300	530	4·76	„

and corrected for the small deviation of steam from the ideal gas law. The third column contains the average of duplicate or triplicate oxygen determinations. The fourth and fifth columns show the flow in ml./min of hydrogen and the addition of a third gas respectively. The values of the apparent equilibrium constants are shown in the sixth column and the last one gives the conditions of preheat for each ingot It can be seen from Table I that the oxygen content of the melt fell in the range 0·03–0·04 % which is high enough for good analytical accuracy and low enough to avoid formation of a non-metallic phase.

The results are shown in Fig. 3 in which the logarithm of the apparent K of eqn (5) is plotted against the reciprocal of the mean square root of the molecular weight of the gaseous mixture. The results fall into three groups with respect

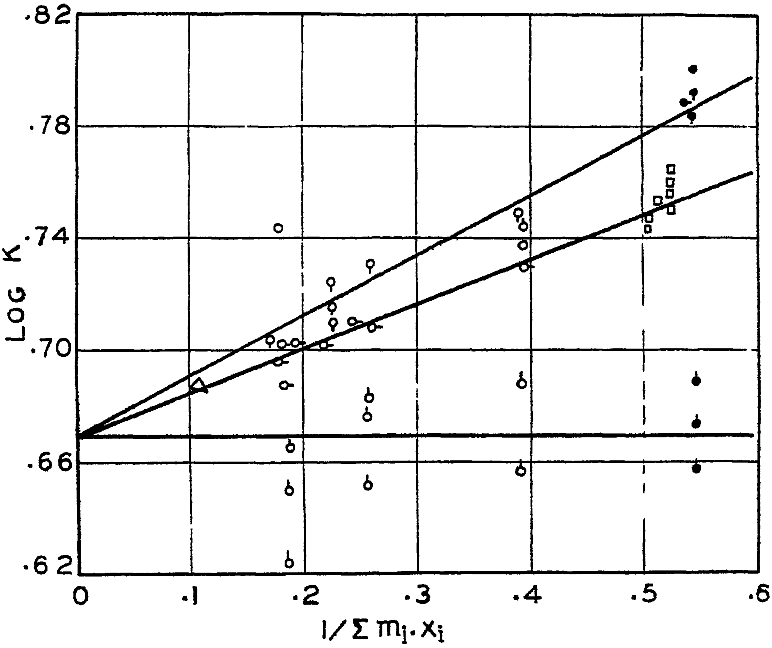


FIG. 3.—Experimental values of the apparent equilibrium constant at 1563° c.

Gas added :	None	Helium	Argon	Hg (mean of 6)
No preheat	●		○	
Low preheat	●̩		o̩	
Intermediate preheat	●-	□	○-	Δ
High preheat	●̍		o̍	

to intensity of preheating of the gas, and include three early results without preheat. Previous results are confirmed in that preheating decreases the apparent value of K, which under a high preheat becomes practically independent of the addition of an inert gas.

Each method of preheating was sufficiently reproducible to establish a constant temperature pattern within the apparatus. Thus $\int d\ln T$ of eqn. (4) was essentially constant for each condition. Fig 3 shows that under such circumstances $\int d\ln(x_{H_2O}/x_{H_2})$ is inversely proportional to $\Sigma m_i . x_i$ as required by the equation. Straight lines may be drawn through the three groups corresponding to the three degrees of preheat.

The effect of adding purified argon is rather striking. Except in the case of high preheat when no temperature gradient existed in the gaseous atmosphere at the liquid metal surface, the argon addition decreased the apparent K by an amount proportional to the reciprocal of the mean root molecular weight. Addition of helium gave results approximately the same as those without admixture, because it does not change $\Sigma m_i x_i$ to any appreciable degree with or without the addition. In one series with intermediate preheat, mercury vapour was added and here the apparent K was the lowest observed for that preheat. The average of six runs is shown as a single point on the plot of Fig. 3.

The numerical value of the equilibrium constant of eqn. (5) is fixed by the experiments at high preheat which yield an average value of 4·70. Even if the preheating had not been adequate the same result would have been obtained by extrapolation of the other lines of Fig. 3 to infinite molecular weight.

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Summary

Thermal diffusion may be a source of serious error in studies of gas-metal equilibria, especially when the metal is heated by induction and sharp thermal gradients are present. It is possible to eliminate the error by adequate preheating of incoming gases. In the absence of sufficient preheat the addition of a heavy inert gas serves to diminish the error. With adequate preheat the results are independent of the amount of inert gas added and when the preheat is inadequate the true equilibrium constant may be estimated by extrapolation to infinite molecular weight.

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GENERAL DISCUSSION

Dr. H. J. T. Ellingham (*London*) (*communicated*) : In his introductory address Sir Andrew McCance has referred to the importance of securing wider and more consistent use of the recommendations in the Report of the Joint Committee of the Chemical Society, Faraday Society and Physical Society on *Symbols for thermodynamical and physico-chemical quantities and conventions relating to their use*, issued in 1937. In this connection it may be of interest to note that these recommendations, with a few minor amendments, were adopted in 1939 by the Royal Society for application in its publications, and were subsequently approved by several other publishing societies in this country. Also, in 1947 the Report of the Joint Committee was taken as the basis of discussion by the appropriate Commission of the International Union of Chemistry, sitting with representatives of the relevant Commission of the International Union of Physics ; the recommendations were again substantially adopted and embodied in a report published in the Proceedings of the 14th Conference of the International Union of Chemistry, 1947, pp. 109–119, and recently approved with minor modifications by the latter Commission. Differences from the recommendations of the original Joint Committee are essentially on matters of detail, especially in the direction of giving additional alternative symbols for certain quantities and a rather wider latitude in respect of certain usages. There now exists, therefore, a broad general agreement among chemists and physicists at an international level on the use of symbols and, what is more important, on the principles governing their use, for it has to be recognised that there is an inadequate number of alphabets and founts to permit restriction of the use of any symbol to a single quantity. It remains, however, to secure agreement with engineering bodies on symbols for quantities, especially thermodynamic functions, of common interest to physics, chemists and engineers, for some of those bodies, particularly in this country, maintain an earlier practice which most publishing societies in other fields have long since abandoned.

Prof. E. A. Guggenheim (*Reading*) said: While full of admiration for Prof. Chipman's masterly review of the available experimental data, mostly emanating from his own laboratory, and for his systematic application of thermodynamics to their analysis, I am somewhat alarmed by his use of the expression "*semi-regular*" solutions. If it is desirable, which I doubt, to use this name at all it is most important that it should be completely and unambiguously defined. Perhaps Prof. Chipman would amplify his definition, which as it stands is somewhat vague.

Prof. Chipman's formula (14) contains a parameter D. If we regard D as defined by this formula, then D is closely related to the osmotic coefficient. The osmotic coefficient g is defined by

$$\mu_i = \mu_i^\circ + gRT \log N_i.$$

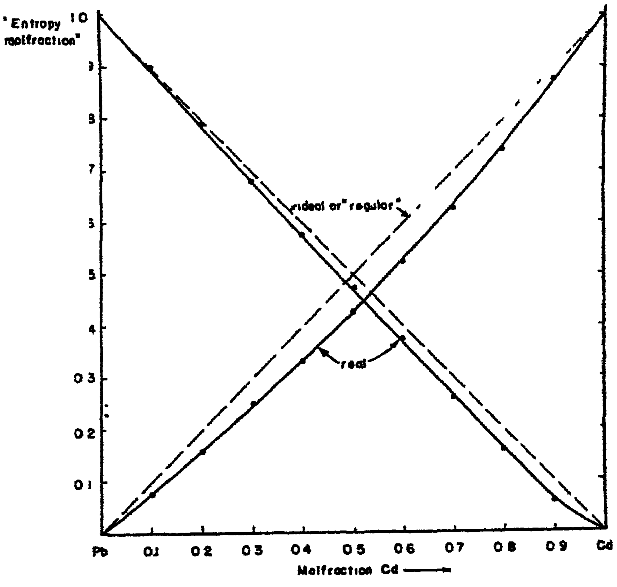
If we differentiate this with respect to T and compare with Prof. Chipman's formula (16) we find that

$$D = g + T\frac{dg}{dT}.$$

Since at any temperature $g \to 1$ as $N_i \to 1$, it follows that $D \to 1$ as $N_i \to 1$. In a regular solution as defined by Hildebrand, including as a special case perfect solutions, D has the constant value unity. In other solutions the value of D varies with N_i. Any constant value of D other than unity would imply such curious properties that I should prefer to call such solutions "*semi-impossible.*"

It is most unfortunate that the same name activity coefficient is used both to measure deviations from Raoult's law (Chipman's γ) and to measure deviations from Henry's law (Chipman's f). It is high time that these two different quantities are given different names. Perhaps one might call the former "fugacity coefficient" and the latter "activity coefficient." To illustrate this terminology let us consider the bismuth amalgams in Fig. 1 of Prof. Chipman's paper, in particular the amalgam with mole fraction 0·5. The fugacity coefficient of the mercury is 0·63/0·50 = 1·26, whereas the activity coefficient is 0·63/0·70 = 0·90.

Mr. O. J. Kleppa (*Chicago*) (*communicated*): The term "regular solution" introduced by Hildebrand is based on the assumption of complete randomness of mixing, and thus corresponds to a well-defined physical model. Such randomness can be strictly fulfilled for an ideal mixture only (Guggenheim [1]). But



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[1] *Proc. Roy. Soc. A*, 1935, **148**, 304.

if the size of the components is approximately the same, and if there is little change in heat content or volume on mixing, the solution will frequently be "regular" with fairly good approximation. Chipman's term "semi-regular solutions" is based on an arbitrary empirical relationship only, and does not seem to correspond to any physical model. The value of such a term appears to be limited.

If it is desired to indicate that the entropy of mixing deviates from that of an ideal (or regular) solution, it should rather be given by a deviation parameter. The parameter given by Chipman (eqn. (14)) does not seem to be the best choice, and the writer suggests as an alternative an "entropy coefficient" δ, defined by the following equation:

$$S_i - S_i^\circ = -R\ln(\delta_i N_i) = -R\ln N'_i$$

The symbols are those used by Chipman. $(\delta_i N_i) = N_i'$ is the calculated mol fraction corresponding to the actual partial molar entropy and might be called the "entropy mol fraction." In the case we have no heat of mixing N_i' would be equal to the activity. For ideal (regular) entropies of mixing δ would have the value 1 for both components over the whole concentration range, while for non-ideal solutions $\delta \rightleftharpoons 1$.

The analogy of this "entropy coefficient" to the activity coefficient introduced by Lewis is obvious, and a graphical representation is equally simple. As an example, I refer to the figure which shows the two "entropy mol fractions" plotted against mol fraction for the liquid system Pb — Cd (data taken from the measurements of Taylor[a]). The system is normally classified as "regular," but the figure immediately shows the deviation. It should be noted that curves *below* the broken lines indicate *positive* entropy deviations.

Mr. T. Rosenqvist (*Chicago*) (*communicated*): In his paper on Activities in Liquid Metallic Solutions, Chipman discusses, among other things, the activity of iron and iron sulphide in the molten part of the system Fe–FeS which he regards as a binary system. The present writer thinks that such a discussion can be done only with certain limitations because the system Fe–FeS is not a complete binary system but only part of the system Fe–S. In the system Fe–S, the relation between the activities of Fe, FeS and the sulphur pressure P_{S_2} is given by the equation:

$$a_{FeS} = K \cdot a_{Fe}\sqrt{P_{S_2}}.$$

(In this equation, $\sqrt{P_{S_2}}$ has been replaced by a_S, the activity of atomic sulphur in the melt.)

The constant K is so chosen that the activity of pure molten FeS is unity. Because the sulphur pressure has a finite value in a melt of stoichiometric composition, the activity of iron must also have a finite value, and cannot as Chipman indicates be zero. The exact value of the iron activity cannot be given at present, but the writer has reasons to believe that it is of the order of magnitude 0·1 at 1600° c.

For comparison, it can be mentioned that in the system silver-silver sulphide, which the writer has investigated,* the activity of silver in molten silver sulphide is found to be 0·92 at the melting point (838° c.) of Ag_2S, decreasing with increasing temperature through a value of 0·73 at 1125° c.

Referred to the quasi-binary system Fe-FeS, the mol fraction of iron will be zero in pure FeS; because the activity of iron has a finite value, the activity coefficient γ_{Fe} will be infinite at this composition. As a consequence, it will be difficult to calculate the activity of FeS by means of Gibbs-Duhem's equation. In Chipman's Fig. 17, the point A would have to be shifted infinitely far to the right and the integrated value for $\log \gamma_{FeS}$ between A and B will be larger than the value given by Chipman. Thus, the values for γ_{FeS} and a_{FeS} will be higher throughout the entire system and a_{FeS} will not follow Raoult's law close to the stoichiometric composition.

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[a] *J. Amer. Chem. Soc.*, 1923, **45**, 2875.

* Paper awaiting publication.

In fact, it is most likely that the activity of FeS plotted against composition will have a horizontal tangent at about the stoichiometric composition. This would be in harmony with the fact that the freezing curve of FeS has a horizontal tangent; the shape of the freezing curve and the activity being interconnected by the equation:

$$\frac{dT_m}{dx} = \frac{RT^2}{\Delta H_m}\left(\frac{\partial \ln a_{FeS}}{\partial x}\right)_{P,T},$$

where X = atomic fraction of iron,
T_m = freezing pt.,
ΔH_m = heat of fusion of FeS.

The best way to obtain more quantitative information about the activities of iron and iron sulphide near the stoichiometric composition is to carry out extended equilibrium studies of the type.

$$FeS + H_2 \rightleftharpoons Fe + H_2S.$$

The writer is at present working on such equilibrium studies and hopes, at an early date, to be able to present the results.

Prof. M. Rey (*Paris*) said: Prof. Chipman made an extraordinarily lucid and forceful presentation of the subject of activities in liquid metallic solutions and made several very interesting contributions to the subject. I was particularly interested in the place which he gave to the use of phase diagrams for the determination of activities as this is a subject which has been almost entirely neglected. For example, Wagner in his important review of the thermodynamics of alloys[3] hardly mentions the method.

In the discussion of the iron-sulphur system, Chipman points out that the activity is exactly known at the liquidus temperature, but that a correction is needed to calculate it for another temperature and that the simplest assumption is that $RT \ln \gamma$ is independent of temperature. This is a characteristic of a regular solution. Therefore the more the solution approaches regularity and the less the temperature differs from the temperature of the liquidus, the more the method of calculation of the activity used here is accurate. It is particularly adapted to systems showing a strong positive deviation and a flat liquidus with a tendency towards immiscibility. A comparison between the activity determined in this way and the activity obtained by other methods is particularly interesting.

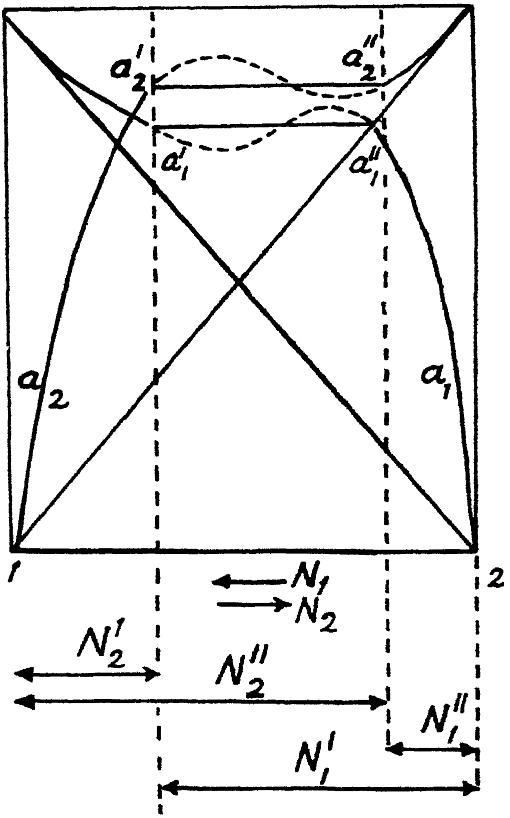

FIG. 1.

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[3] Cp. Masing's *Handbuch der Metallphysik* (Leipzig, 1940), Vol. I, Part III.

It is gratifying to note the agreement observed in the iron-sulphur system between this method and chemical equilibrium with hydrogen-hydrogen sulphide mixtures.

Lumsden showed in his paper on the zinc-cadmium system [4] that such an agreement existed between the activities of zinc measured by the potentiometric method by Taylor [5] and those deduced from the phase diagram, assuming $RT \ln \gamma$ to be independent of temperature. I carried out the same calculations for the lead-cadmium system and found a similar agreement between the figures of Taylor and those deduced from the phase diagrams. In the zinc-tin system, however, it was impossible to obtain agreement, even when using equation (11) of Chipman and the values of the heat of mixing of Kawakami. I have therefore doubts as to the correctness of the measurements of Taylor in this case.

Another method of obtaining activity curves from a phase diagram is the use of a gap in miscibility. In that case the activity of a given constituent is necessarily the same in the two liquid phases which are in equilibrium. The activity curves of constituents 1 and 2 are as shown in Fig. 1. These activity curves can usually be represented by equations of the form [6]:

$$\log a_1 = \beta N_2^2 + \gamma N_2^3 + \log N_1 \quad . \quad . \quad . \quad (a)$$

$$\log a_2 = (\beta + 1{\cdot}5\,\gamma) N_1^2 + \gamma N_1^3 + \log N_2 \quad . \quad . \quad . \quad (b)$$

The two activity curves are completely determined by the values of the parameters β and γ and the Gibbs-Duhem relation is implicit in these equations.

In Fig. 1 the dotted lines represent parts of the curves which have only virtual existence. Now by writing:

$$a'_1 = a''_1 \text{ and } a'_2 = a''_2$$

two equations are obtained which permit the calculation of the parameters β and γ. The two activity curves are therefore completely determined if the gap in miscibility is known and if the activity curves can be represented by equations such as (*a*) and (*b*).

I applied this method to the Pb–Zn diagram using the data of Waring which were used also by Lumsden. The activity of zinc in lead in the miscibility gap was found to be 0·94, checking exactly with Fig. 7 of Mr. Lumsden's paper. However, the curve obtained on the lead side differed somewhat from his curve and the activities were higher.

It is not certain whether equations as simple as (*a*) and (*b*) can represent the activities very accurately in the present case. The matter warrants further study and in this connection it would be worth while if Mr. Lumsden would explain his method of calculation in more detail.

Mr. J. Lumsden (*Avonmouth*) said: In a dilute solution, the thermodynamic potential of the solvent, referred to the pure liquid, is given by the equation

$$\mu_A - \mu_A^0 = RT \ln N_A + bN_B^2, \quad . \quad . \quad . \quad (1)$$

with $N_B \ll 1$ and where b is a constant for the particular solvent A and solute B. Eqn. (1) is useful for determining entropies of fusion from depressions of freezing-points when there are appreciable deviations from Raoult's law. When the pure solid solvent separates, the following equation is satisfied,

$$-\frac{RT \ln N_A}{T_M - T} = \Delta S + b\frac{N_B^2}{T_M - T}, \quad . \quad . \quad . \quad (2)$$

where T_M is the melting point of pure solvent A, T is the liquidus temp. for a solution containing a mole fraction N_A of A, and ΔS is the entropy of fusion of A. Hence, by plotting,

$$y = -\frac{RT \ln N_A}{T_M - T} \text{ as a function of } x = \frac{N_B^2}{T_M - T},$$

there is obtained a straight line which intersects the axis $x = 0$ at the point $y = \Delta S$.

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[4] *Congr. Pure Appl. Chem.* (London, July, 1947).

[5] *J. Amer. Chem. Soc.*, 1923, **45**, 2865.

[6] These are derived from eqn. (13) and (14), p. 44 in Hildebrand's *Solubility of Non-electrolytes.*

This procedure for calculating entropies of fusion, which has not been widely applied to metals, has the advantage that the test of linearity provides an internal check on the accuracy of the experimental data. In practice, the scope for such calculations is limited by the lack of accurate data. Heycock and Neville carried out determinations in which lowerings of freezing-points of metals were measured to 0·01° C., and an examination of their results generally shows an internal consistency well within 0·05° C. for each binary system. For the same solvent with different solutes, the results are very consistent in cases where solid solubility is negligibly small or where it is appreciable, but allowance is made for it. Further confidence in the accuracy of their results is derived from the fact that they give for the heat of fusion of cadmium 1500 cal./g.-atom, which may be compared with the calorimetric value of 1530 ± 70 reported by Kubaschewski and Huchler [7] For lead, similar calculations lead to a heat of fusion of 1090 cal /g -atom, which is regarded as more accurate than any of the calorimetric determinations.

Heycock and Neville measured freezing-point lowerings more accurately than their absolute temperature. Since the time of their work, interest in freezing-point lowerings, as such, has lapsed, and liquidus temperatures near the composition of one component have been reported only as accurately as the temperatures themselves could be determined, that is, to the nearest 1° C. or occasionally 0·1° C. Such results cannot form a basis for the accurate estimation of heats of fusion.

In eqn. (1), the parameter b may vary with temperature. Let

$$b = b_0 - aT, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where T is the temperature in ° K. Then the partial molal entropy and heat content of the solvent, referred to the pure liquid, may be written, respectively,

$$S_A - S_A^\circ = R \ln N_A + aN_B^2 \quad . \quad . \quad . \quad (4)$$

and

$$\bar{H}_A - H_A^\circ = b_0 N_B^2. \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Eqn. (4) and (5) are generally valid only for dilute solutions. With non-polar components of equal molecular volume, (5) is valid for all concentrations, provided that the two species are randomly distributed. It has sometimes been stated that for such solutions the entropy of mixing must be ideal. This, however, is not necessarily so, and, in the case of liquid alloys, non-ideal entropy of mixing is the rule rather than the exception.

In liquid metals, the thermal motions are essentially vibrational, so that the vibrational partition functions of the solution and of the pure components have to be taken into consideration in calculating the entropy of mixing. Only if the effective mean vibration frequency in the solution is equal to the weighted geometric mean of those in its components will the entropy of mixing be ideal. Provided that the ratio of the characteristic frequencies involved is not large, this means that the ideal entropy of mixing is to be expected only if the rate of variation with distance of the force between a pair of unlike atoms is the geometric mean of those between the two pairs of like atoms. To explain the entropies of liquid alloys, it must be assumed that this simple geometric mean rule for the potential between unlike atoms is not generally satisfied except for closely similar metals such as zinc and cadmium.

Sir Charles Goodeve (*B.I.S.R.A., London*) (*communicated*): Kitchener, Bockris and Liberman measure the " increase in the activity " of sulphur caused by the presence of carbon. Strictly speaking, they mean an increase at constant sulphur concentration. In their discussion they refer to " the carbon and sulphur competing for iron atoms . . . " It is suggested that the theory would follow easier if, in the first place, they said that at a given sulphur potential or activity the " capacity " of iron for sulphur is reduced by the presence of carbon, a fact which follows at once from Fig. 5.

Prof. J. Chipman (*Cambridge, Mass.*) said: In addition to the published data on the activity of sulphur in liquid iron, etc., which Dr. Kitchener *et al.* have reviewed, there are two as yet unpublished researches which may be mentioned for the sake of comparison. J. P. Morris and A. J. Williams of the U.S. Bureau of Mines, using a new technique, find for the ratio $p_{H_2S}/p_{H_2} . \% S$ at low sulphur contents and at 1615° a value of about $2{\cdot}6 \times 10^{-3}$. This is somewhat lower than the "carbon-free" values reported by the authors for 1570° despite the higher temperature. The lower value is confirmed by the recent determinations of H. Elvander in the writer's laboratory. This suggests that there may be a greater difference between the carbon-saturated and the carbon-free ratios than that shown in Fig 5 and hence a greater effect of carbon upon the activity of sulphur. Morris and Williams also studied the effect of silicon and found that the activity coefficient of sulphur was about doubled by 4 % silicon; it was increased 5- or 6-fold by 9 %. This is a much greater effect than that reported here for carbon.

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[7] Kubaschewski and Huchler, *Monograph KWI Metallf.* (Stuttgart); *Tech. Inf. Bur. TPA* 3 (Translation No. CoDC/206T).

Dr. P. Herasymenko (*Sheffield*) said: The results of the work of Kitchener, Bockris and Liberman show that carbon increases the activity of sulphur in molten iron. One may expect that carbon will produce a similar effect on the activity of oxygen in steel. In the paper published last December in the *J. Iron Steel Inst.* I have shown with data from the acid open-hearth furnace, that carbon increases the activity of oxygen.

This result is in disagreement with the deductions of Marshall and Chipman,[8] who thought that the activity coefficient of oxygen in liquid steel is lowered by carbon and, therefore, the product [C] [O] increased with increasing carbon content. The deductions of Marshall and Chipman cannot be, however, regarded as certain.

These authors made their measurements on melts heated by induction in magnesia crucibles in a closed furnace at various pressures of $(CO + CO_2)$ mixtures. After taking the gas samples for the determination of equilibrium gas composition, aluminium was added to the melt: the power was switched off 30 sec. after aluminium addition, and carbon and oxygen were determined in the solidified metal. During the time allowed for aluminium to mix thoroughly with the melt, the aluminium could react not only with oxygen dissolved in the bath, but also with iron oxide adsorbed and absorbed by the surface layers of magnesia crucible. The determined oxygen contents were probably too high, and, therefore, the conclusions of the authors on the decrease of the activity coefficient of oxygen in the presence of carbon are not convincing. (The conclusions with regard to the activity of carbon—derived from the same experiments and cited by Prof. Chipman in this Discussion—were not, of course, affected by the mode of killing the steel.)

A re-investigation of the carbon-oxygen equilibrium is desirable. At present it seems to be safer to accept the equilibrium constant as derived by Vacher and by Phragmen and Kalling although even this value may be somewhat high at high contents of carbon.

Dr. F. D. Richardson (*B.I.S.R.A., London*) (*partly communicated*): In connection with the papers by Prof. Chipman, and by Dr. Kitchener, Dr. Bockris and Mr. Liberman, I would like to call attention to the mutual effects of various solutes in liquid iron. Fig. 26 and 28 of Prof. Chipman's paper show that carbon, silicon and phosphorus increase the activity coefficients of each other when in solution together. Dr. Kitchener's paper shows that carbon increases the activity coefficient of sulphur markedly, and information is now available that silicon behaves in a similar manner. On the other hand there is good evidence from the work of Prof. Chipman and his co-workers,[9] that carbon *lowers* the activity of oxygen. Further, the work of Zappfe and Sims [10] indicates that silicon behaves in the same way. The similarity between oxygen and sulphur would, however, lead one to expect an increase and not a decrease in the activity of oxygen under these conditions.

In seeking an explanation of these effects it is necessary to consider the manner in which these solutes exist in liquid iron. In the solid state, carbon in γ-iron is present in the octrahedral interstices and is co-ordinated with six nearest iron atom neighbours. In molten iron, except for the general disorder peculiar to the liquid, its situation must be much the same and similar conditions must apply to other non-metallic solutes. If a pair of such solutes compete for the same octrahedral spaces, a mutual increase in their activity coefficients will result. If, however, they can become associated by entering into each other's co-ordination shells, and if this associated state has a lower energy than that of the two atoms co-ordinated separately with the iron, a mutual lowering of activity coefficients will result.

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[8] Marshall and Chipman, *Trans. Amer. Soc. Met.*, 1942, 30, 695.

[9] Marshall and Chipman, *Trans. Amer. Soc. Met.*, 1942, 30, 695.

[10] Zappfe and Sims, *Trans. Amer. Inst. Min. Met. Eng.*, 1942 (Tech. Publ. 1948).

The elements which are likely to cause a decrease in this way are those which are known to form stable associations under other conditions. On this view, the difference in the behaviour of oxygen and sulphur can be related to the stability of CO and SiO relative to CS and SiS. On the other hand, pairs of solutes which carry charges of opposite sign when present separately in solution, would similarly be expected to associate, and pairs with similar charges to show the reverse effect. It is of some interest, therefore, to consider from this standpoint also, the manner in which such solutes as carbon and oxygen are present in liquid iron.

Dr. Kubaschewski has referred to the evidence which shows that carbon exists in γ-iron as a positively charged entity,[11] or at least parts with an electron readily enough to migrate as a positive ion. It doubtless behaves similarly in liquid iron. Those properties of the carbon atom which have a bearing on this behaviour and have been determined are the ionisation energy and the electron affinity. These have, therefore, been tabulated below for carbon and the other atoms of interest here, the electron affinities quoted being the empirical extrapolated values given by Massey.[12]

Ionisation Energy (kcal.) $X \rightarrow X^+$		Electron Affinity (kcal.) $X \rightarrow X^-$	
C	—251	C	31
Si	—182	Si	—
P	—256	P	3
O	—303	O	85
S	—231	S	47

Oxygen which has a much greater electron affinity and a greater ionisation energy than carbon should be negatively charged when dissolved in liquid iron, and should show a significant degree of association with the dissolved carbon. Similar considerations are likely to apply in the case of oxygen and silicon. For sulphur the values of the electron affinities and ionisation energies are more similar to those of carbon than of oxygen, so that sulphur may be neutral and even positively charged, and should thus show no tendency to associate with carbon or silicon.

In whichever way the results are regarded, I do not feel it is reasonable to endeavour to interpret this lowering of the activity coefficients of oxygen in terms of concentrations of CO and SiO which are supposed *not* to influence the activity coefficients of those solute atoms which remain separate from each other. In so far as these associations are themselves co-ordinated with considerable numbers of iron atoms, they must increase the activity coefficients of the remaining solute atoms and thus cause effects which are rather more complex. This seems to be the most probable explanation of the failure of Zappfe and Sims to find sufficient oxygen in their melts to account for the SiO concentrations which they calculated, on the assumption that the activity coefficients of the "free" [Si] and [O] were independent of the overall concentrations.

Dr. J. White (*Sheffield*) said : In their paper Dr. Kitchener, Dr. Bockris and Mr. Liberman comment somewhat reproachfully on the fact that Dr. Skelly and I did not plot our results in a way which would have revealed the variation of the activity coefficient of the sulphur in the iron with sulphur content. At the time we regarded our data as incomplete and the experimental error uncertain due to the fact that the work had to be terminated prematurely when both Dr. Skelly and I left Glasgow. The paper was actually written early in 1943, though it was not published until 1947, and at that time, though we were aware of the non-ideality indicated by the form of the liquidus curve of the Fe-S system, we should, I think, have been rather hesitant to explain away the variations in the constant by invoking a variable activity coefficient.

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[11] Seith and Kubaschewski, *Z. Elektrochem.*, 1935, 41, 551.

[12] Massey, *Negative Ions* (Cambridge Univ. Press, 1938, p. 15).

We were also somewhat disconcerted by the rather large and variable silicon content which we found in our melts, and which, we suspected, was tending to raise the value of the constant. (Our constant was the reciprocal of that defined by the present authors.) Such an effect is consistent with an increase in the activity coefficient of the sulphur in the metal with increasing silicon. Further, as examination of our results will show, there was a general tendency for high silicon to be associated with low sulphur and vice versa, so that the change in the value of the constant with increasing sulphur content could, or so it appeared to us then, be attributed to the effect of decreasing silicon content. In view of this we are naturally interested in the information just given by Prof. Chipman that, at higher concentrations at least, silicon does increase the activity coefficient of the sulphur.

We are particularly interested to find that the authors have adopted the technique of using a small metal bead in an even smaller reaction chamber than we used. If I have any criticism to make, it is that in allowing the gas to escape from the reaction chamber into the wider tube they will tend to promote sulphur deposition from the outgoing gases. In view of the difficulties associated with the use of H_2–H_2S atmospheres we found that comparison of ingoing and outgoing gas compositions provided a valuable check on the performance of the apparatus. I do not suggest, however, that the validity of their data is in question because they have omitted to make such a check.

Dr. J. A. Kitchener (*London*) said : Dr. Richardson has pointed out that, whereas carbon *increases* the activity of sulphur, silicon and phosphorus in liquid iron, carbon and silicon appear to *decrease* the activity of oxygen. Prof. Chipman has referred to unpublished work in which silicon has been found to increase the activity of sulphur. Accepting the observations on oxygen (although several speakers have questioned them), it is interesting to consider the structural cause of the different behaviour of oxygen.

Reduced activity in solution generally indicates tendency to compound formation. When two solutes, A and B, are dissolved in liquid iron the influence of A on B will depend on the relative " affinities " of A — B, A — Fe, and B — Fe. Where the last two are strong compared with the first, then A and B will compete for iron, and this will result in a " repulsion " of one another (as in Fe — S — C). Where the affinity of A for B is larger than that of A and B for Fe, there will be a reduction in activity of both. It seems plausible to suppose that this is so for the pairs C — O and Si — O. The stability of fayalite (Fe_2SiO_4) strongly supports this view. Dr. Bockris points out that the structural cause of the difference is probably the small size and high electronegativity of oxygen.

The final answer to Dr. Richardson's question can only come from a more detailed knowledge of the structure of these semi-metallic solutions. This leads to the point raised by Dr. Anderson, who thinks that an ionic model for sulphides (such as that discussed in our paper) is dubious. The precise extent of electrovalency and covalency even in pure crystals is, of course, at present uncertain. No doubt sulphides are " more covalent " than oxides, but since most salts are supposed to lie somewhere between the two extremes,[18] and since evidence referred to in our papers indicates that many such melts are probably electrolytic conductors, we are justified in using ions as a very reasonable and prominent canonical structure in discussing the behaviour of sulphide melts. The problem is complicated in the present system by the fact that Fe–FeS mixtures are partially metallic and partially ionic—a type of system which appears to have been little studied in the past.

In reply to Dr. Anderson, although the solutions used in our work contained only a few per cent. by weight of solute they were, in fact, relatively concentrated

[18] Pauling, *Nature of the Chemical Bond.*

owing to the disparities in atomic weights. Thus, 5 % carbon in iron corresponds to 20 atomic %, and it already reduces the activity of Fe to 0·6 compared with unity for pure Fe. It might be a useful practice (as has been recommended to me by Prof. Guggenheim) for authors of papers of this kind to always present tables or graphs of data with *both* weight and atomic percentage scales.

We thank Prof. Chipman and Dr. White for their remarks. In reply to the latter, we were not interested in analysing the exit gas in our experiments as the use of a carbon capillary tube as inlet ensured a rapid (linear) rate of streaming, thus eliminating thermal diffusion and reaction with silicate refractories. In this way we could be confident that the sample was bathed in a gas mixture identical with that *entering* the furnace.

We concur with the remarks of Sir Charles Goodeve, and can now add (from recent results) the parallel statement that the capacity of liquid iron for carbon (i.e., solubility) is reduced by the presence of sulphur—as predicted in our paper

Dr. O. Kubaschewski (*Teddington*) (*communicated*) : Mr. Lumsden's paper represents doubtless the best and most detailed evaluation of the phase boundaries and thermodynamics of the system under consideration. A similar evaluation has been carried out recently by Scheil.[14] Using only the data of Haas and Jellinek for the miscibility gap he obtained a curve for the heat of mixing which agrees very well with Kawakami's values except for the composition $N_{Zn} = 0{\cdot}07$. Waring's curve for the miscibility gap may, however, be more reliable. It must be emphasised that the direct experimental determination of heats of formation of alloys is subject to an appreciable error even with the best techniques at present available. Some work of this kind has been carried out at the KWI, Stuttgart, where it was generally assumed that the limits of error were ± 6 % for heats of formation of the order of 2000 cal For smaller heat effects the percentage error is even higher. We may accept Kawakami's results as being correct within 100–250 cal. (in case of alkali metal alloys they are higher). The calculation applied to the lead-zinc alloys should be more accurate than the determination. Calculation, however, often involves assumptions concerning ideal behaviour which may also involve an appreciable error. It must be emphasised that the accuracy of thermochemical data is much too often overestimated and thus causes scepticism toward thermochemical calculations among those who wish to apply the data to practical problems.

Concerning the heat of fusion of zinc, the value given (1740 cal /g.-atom) is in very good agreement with the value 1720 cal. which we determined recently by heat content measurements. For that of lead I should still prefer the mean value 1190 ± 30 cal./g.-atom obtained from good calorimetrical and other measurements, instead of the value 1080 derived by Lumsden from freezing-point lowering. The latter method is valid only under conditions of ideal behaviour, and is very sensitive toward inaccuracies in the temperature measurements.

Dr. R. M. Barrer (*London*) said : Gases and metals may react to give oxides, sulphides, nitrides and the like which show little or no structural or chemical similarity to the parent metal. The properties of such compounds are of major importance in chemistry and metallurgy.

The present paper, however, describes a less well-known association between non-metal and metal, which is also important in some metallurgical processes. If the non-metallic element is small enough, it may enter the interstices of the metallic crystal without destroying its metallic conductivity and without greatly modifying the original arrangement of the atoms in the metallic crystal.

The properties associated with some of these interstitial solid solutions, in both equilibrium and kinetic aspects, merit close attention and much remains to be done before any full understanding of them is obtained. At least two general criteria for their formation exist :

(1) a suitably small radius ratio of non-metallic element X to metallic element A, to enable X to fit interstitially in the metallic lattice ;

(2) a reasonably small difference in electronegativity of X to A so that electron transfer and the formation of ionic lattices is not preferred as the more stable state

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[14] Scheil, *Z. Elektrochem.*, 1943, **49**, 250.

Our knowledge of the bond in these metallic interstitial solutions is imperfect; as indeed is understanding of the metallic bond in general. Thus the current view of a metal crystal as a set of positively charged ions in a sea of conductivity electrons, while able to explain some features of metal physics, seems less suited to explain the great hardness, refractivity and chemical inertness of some metallic crystals. Accordingly a "chemical" theory of the metallic bond, due to Pauling, has been referred to in discussing the bond in what are often quite extraordinarily hard, high-melting, inert but electronically conducting interstitial solutions. It is an obvious task of metal chemists to go beyond the phenomenology and thermodynamics of metal behaviour and attempt interpretations here as in other domains of physical chemistry.

Equilibrium between gas and metal can be satisfactorily formulated by statistical methods in favourable cases; it must be emphasised that, as yet, this formulation introduces the energy of solution without describing its origin. Therefore it offers so far no comment on the nature of the bond. It is, however, found that where the element X is diatomic in the gas phase it exists as discrete atoms in the metallic interstices, in which the atoms behave as oscillators.

Energy fluctuations endow the oscillator at times with enough energy, E, to render it mobile, so that if a vacant interstice is present adjacent to it, it may move to the vacant site and so diffuse slowly from point to point. The chance that an adjacent vacant site occurs is $(1 - \theta)$, where θ denotes the fraction of all available interstitial sites occupied by atoms X. Then in an ideal * interstitial solid solution the diffusion coefficient D, for X, will be governed by two laws:

$$D = D_0 e^{-E/RT} \quad \text{(law of temperature dependence)}$$

$$D = D_1(1 - \theta) \quad \text{(law of concentration dependence).}$$

The first law has been abundantly verified. The second law holds for some gas-zeolite systems (which provide a very simple type of interstitial solid solution); but little evidence yet exists to test it for metallic interstitial solutions. Owing probably to departures from the ideal the C-Fe system does not appear to follow the concentration law, although D does depend on the carbon content.

Concentration dependence of D requires generalisation of the diffusion equation to $\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right)$. Still further one may assume that free-energy gradients produce diffusion and give as the fundamental diffusion equation in the x-direction:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D_1\frac{\partial a}{\partial x}\right) \qquad D_1 = \frac{DRT}{\gamma}$$

$$(a = \text{activity}).$$

In this field, and in the allied field of diffusion in multi-component systems, little quantitative progress has been made, although much interest must attach to comprehensive determinations of the concentration dependence of D in alloy systems.

Among the complicating factors arising when gases diffuse in metals are slow phase-boundary reactions which may govern the rate of permeation through the metal, if the transport of gas through the surface layer is slower than interstitial diffusion within the metal. Possible phase-boundary processes have therefore been formulated and a description has been given of *one* line of approach to determine whether it is these processes or diffusion which set the tempo of permeation through metallic membranes. In this field, as in others referred to earlier, results are so far incomplete. There eventually may prove to be a relation between slow surface processes and catalytic activity, for both in turn depend upon the previous history of the surface, the presence of poisons and the degree of sintering of the surface.

Mr. K. H. Jack (*Cambridge*) said: In discussing the conditions for formation of interstitial phases, Dr. Barrer points out that expansion or distortion of the metal lattice is likely for radius ratios above 0·41, but according to accepted views,(1) * expansion also occurs when the radius ratio is less than 0·41. Whatever the value of the radius ratio, it is a necessary condition for the existence of an interstitial phase that the non-metal atom occupies the particular type of interstice, tetrahedral or octahedral, in which it can maintain contact with its metal-atom neighbours. In general, the non-metal atom is larger than the available interstice of the undistorted metal-atom lattice, so that when this interstice is occupied the metal atoms are forced apart and, even in an " ideal " interstitial solution, they no longer remain in direct contact with one another. This point is important since it implies that there is a strain energy contribution to the free energy of each interstitial phase.

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* In the sense that introducing the interstitial atom causes a negligible distortion in the parent metal crystal.

There is a gradual increase in unit cell dimensions as the interstitial atom concentration increases. The limit beyond which a simple metal-atom lattice cannot be expanded was found empirically by Häag (1) to correspond with a critical radius ratio of 0·59, using the ordinary covalent values for the radii of the interstitial atoms. An attempt to justify theoretically a limiting value of 0·59 is not consistent with values of radius ratios given in Table I of Dr. Barrer's paper, since if these latter are used, the observed limit is not less than 0·63. In any case, I do not know of any interstitial phase which has a special structure where the non-metal atom has a co-ordination number 7 or 8. For example in cementite, where the critical radius ratio is exceeded and which has a complex structure, a co-ordination number 6 is still maintained.

NATURE OF INTERACTIONS BETWEEN METAL AND INTERSTITIAL ATOMS.—In the Pd-H system, Coehn and Specht (13) observed qualitatively the presence of cationic hydrogen, while in a quantitative investigation Duhm (13) obtained a value $+e/500$ for the average charge on each hydrogen atom. A mistake in calculation was subsequently pointed out[15] which on correction gave a value $+e/25$. Considering that the movement of positive hydrogen will be retarded by the metallic electrons, this evidence for the existence of cationic hydrogen in Pd cannot be neglected. Lacher (16) suggests that the dissolved hydrogen is almost completely ionised, the electrons going into the $4d$ shell. To account for the existence of a hydrogen-rich and a hydrogen-poor phase in equilibrium (i.e., the existence of a miscibility gap below a critical temperature and below a critical hydrogen pressure), it is not necessary to assume as Lacher did that " the protons with their compensating atmosphere of negative electrons must attract each other according to some unspecified law of force." The problem is the general one of uphill diffusion to which Dr. Barrer refers in his final section.(34) An interstitial atom or a substitutional solute atom distorts the metal-atom lattice, and one solute atom strains a relatively large number of surrounding unit cells of metal atoms in which solute atoms are absent. At a given concentration, the strain energy will be a maximum when the solute atoms are widely dispersed but may be reduced if all the expanded solute-containing unit cells occur as one crystal and all the solute-free unexpanded cells form a separate crystal. In other words, the strain energy is one of the factors which might explain why a two-phase system (e.g., α and β Pd–H; α and α' Fe–Cu–Ni) is of lower free energy under certain conditions than a one-phase system. With increasing temperature, thermal energy will reduce the relative strain energy contribution so that the miscibility gap will shorten until it disappears at a critical temperature when the normal tendency for solute atoms to achieve maximum separation becomes dominant. This is exactly what is observed for Pd–H and for Fe–Cu–Ni.

Fowler and Smithells (18) consider that hydrogen dissolved in Fe, Co, Ni and Cu is present in the form of protons, the extra electrons being distributed with the metallic electrons in the usual bands. It is inferred in the present paper that Pauling's conception of metallic binding can be applied to interstitial alloys. Such a conception of resonating one-electron or two-electron bonds is merely another way of expressing the older idea that the valency electrons are shared between all the atoms. It does not invalidate the simple conception that a metal can be regarded as an array of positive ions held together by attractions to the common system of negatively charged electrons.[16] Both concepts are probably equally crude. By applying Pauling's ideas to interstitial alloys we imply that the bonding between metal and non-metal atoms is the same as that between metal atoms. If this is so, then equally well we can consider the interstitial atoms to behave like metal atoms. That is, they contribute electrons to the free electron gas and behave as if they carry some positive charge. Since only those metals with incomplete *d* shells form true interstitial alloys, it is possible that the electrons contributed by the interstitial atoms are shared between these *d* " holes " and the free electron gas. The electron contribution by the non-metal and the proportion going into the *d* shell will both vary from system to system, which might account for the wide variation in properties among interstitial structures. I have attempted to apply Pauling's calculations for determining bond lengths in the systems Fe–N, Fe–N–C, Ni–N, Ni–C, Ni–N–C and Ti–C, so far without success, and I feel that their unmodified application to all classes of interstitial structures is impossible.

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[15] Duhm, *Z. Physik*, 1935, **95**, 801.

* Numbered references in parentheses are those given in Dr. Barrer's paper.

Rundle (14) states that uranium hydride (UH_3) is unique and " in no sense of the word can it be thought of as an interstitial solution." Metal-metal bonds of any strength are almost completely lacking so that UH_3 cannot be compared with an interstitial hydride.

CONCENTRATION DEPENDENCE OF THE INTERSTITIAL DIFFUSION COEFFICIENT.—Because the observed variation of diffusion constant with concentration for carbon in γ-iron is not in agreement with eqn. (18), it cannot be argued that austenite is not an ideal interstitial alloy. Data of Wells and Mehl (32) were obtained under experimental conditions such that only austenite was present, and so consideration of possible complications due to ferrite, martensite or cementite is unnecessary. The strain factor described above might explain, however, the observations. The carbon atoms of austenite expand not only the interstices which they occupy but also many of those which are vacant. It will be much easier for a carbon atom to move from hole to hole where these holes are already expanded by the presence of neighbouring interstitial atoms. Hence, the diffusion constant will increase with concentration. In a similar way, the presence of foreign atoms such as Mn and Ni will distort the lattice and increase the diffusion constant of carbon, in agreement with observations. Moreover, diffusion constants of Ni and Mn in γ-iron increase with increasing Ni and Mn concentrations. Ni and Mn form substitutional solid solutions, but at low concentrations of solute the argument applies equally to both types of solution. With increasing solute concentration the proportion of available unoccupied interstices ($1-\theta$) may become an increasingly important factor in the case of interstitial solutions, so that we might expect the diffusion constant to increase at first and then decrease at high concentrations. In the above examples, which are the only metal systems so far studied, the maximum solute concentration is not large enough to test the validity of this idea.

Dr. R. M. Barrer (*London*) (*communicated*) : Mr. Jack's opinions as to the nature of the bond are well-known standard views based on the Bloch theory of metals. Until recently this was the only treatment possible, but as I have explained, one may now develop a second theory based on Pauling's idea of the metallic state which seems better suited to explain such physical properties of interstitial solutions as their hardness and refractivity. A similar point of view has been developed independently and in greater detail by Rundle[17] for interstitial carbides, nitrides and oxides of composition MX, in a paper which has appeared subsequently to my contribution to this Discussion. He has shown a number of advantages of the resonating electron-pair bond theory as a means of describing these phases.

It is not possible to sustain a view of dissociation of interstitial H-atoms into free electrons and protons on any existing data, for if the association between so-called " screening " electrons and protons is so intimate that the effective charge on the proton is only 0·04 of the normal charge then it is meaningless to speak of the H-atoms as dissociated in the usual sense.

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[16] See Hume-Rothery, *Atomic Theory for Students of Metallurgy* (The Institute of Metals, 1946), p. 147.

[17] *Acta Cryst.*, 1948, 1, 180.

Strain energy is a part only of the normal interaction energy when the primary X-A bonds form. Strain energy must not be considered separately from entropy and other energy effects which together give the free energy of formation which alone determines the stability. Whether strain energy could account for the formation of α- and β phases in H-Pd is, at present, speculative.

As regards the concentration dependence of the diffusion coefficient, it may well be that few, if any, metallic interstitial solutions are ideal in my sense of showing no expansion of the metallic lattice when the atom X enters it. In this case the effect of expansion upon the diffusion coefficient is a general factor, as well as the factor $(1 - \theta)$ due to increasing concentration of interstitial atoms. It must be left to subsequent measurements to reveal the interplay of these factors.

Dr. J. O'M. Bockris (*London*) (*communicated*): In connection with the remarks of Barrer and of Jack on the Pd–H systems, it may be noted that Frumkin and Aladjalowa[18] have recently applied hydrogen overpotential charging-curve measurements to the systems and have been able by this means to examine phase transitions. Herringshaw, Bockris and Fleischmann are investigating several metal-gas systems by a similar method at Imperial College.

Mr. D. W. Hopkins (*Swansea*) (*communicated*): The paper by Kitchener and Bockris will be received by experimentalists wishing to study reactions at temperatures over 1600° c. as a substantial contribution to knowledge. The full and lucid description and directions for operating enhance the value of the paper by making it of immediate practical value. It is felt, however, that more can be said in favour of the commonly installed high-frequency furnace—35kva, 20,000 cycle, spark-gap oscillator. The dimensions and frequency limit its use as installed to a minimum size of charge roughly equal to a 1 in. diam. bar of metal, if the usual refractory crucible is used, but this minimum can be lowered if the material to be melted is contained in a graphite crucible, or a special refractory crucible within one of graphite. But there is a minimum size here also and there are difficulties due to the reducing atmosphere. A considerable improvement may be effected by replacing the normal sillimanite crucible by an alumina tube of 4 in. bore which has an internal liner of graphite 1 in. thick and 6 in. long. An inner alumina tube may be heated by this means to 2000° c. with a controlled internal atmosphere. For very small charges, in our case of the order of 0·125 in. diam. and 3 in. long, we have constructed auxiliary heating coils of copper tube which are 2–2·5 in. diam. and 4–6 in. long. They contain 15–25 turns of 0·25 in. diam. tube around the silica sleeve which, in turn, contains an inner alumina tube, insulated by zirconia powder. Small coils of this kind will not resonate unless placed in series with the main coil and there is a maximum electrical capacity, equal to about a quarter of that of the main coil, above which it is not possible to operate. From the above, it may be seen that charges weighing from a few grams to 18 lb. can be handled with little trouble and trifling expense, while retaining all the advantages listed by the authors.

Dr. O. Kubaschewski (*Teddington*) said: Dr. Kitchener and Dr. Bockris point to the limits of usefulness of platinum furnaces above 1500° c. due to a rapid evaporation of platinum. Actually this becomes dangerous even below 1500° c. It should be emphasised that this loss of metal is not due to the evaporation of pure platinum; the vapour pressure is only 10^{-4} mm. Hg at 1700° c. Platinum however, tends to form gaseous oxides, the formation of which results in the loss of metal. This oxide formation becomes noticeable at 1100° c. and increases rapidly above this temperature. It has been confirmed frequently[19] that platinum evaporates in presence of air or oxygen but does not do so in pure nitrogen or argon. Therefore one should recommend the complete exclusion of oxygen from contact with the winding in platinum furnaces. Then, however, there is no greater advantage to molybdenum furnaces.

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[18] *Acta Physicochim.*, 1944, **19**, 1.

[19] e g., Fröhlich, *Degussa Metallbericht*, 1941, **109**, 112, 123. Schneider and Esch, *Z. Elektrochem.*, 1943, **49**, 55.

Mr. L. R. Barrett (*London*) said : I should like to offer the following points for consideration. One of the greatest needs in high-temperature research is for controllable high temperatures in oxidising conditions. These conditions are not easily attainable above about 1600° c., because a refractory tube impermeable to hydrogen is not available to separate the hydrogen atmosphere necessary with molybdenum and tungsten furnaces.

Are the long periods of running-in of molybdenum tubes furnaces really necessary ? No one seems to know whether this requirement is occasioned by the alumina tube or the molybdenum wire.

During the last fifty years, there seems always to have been a hope that some unfamiliar refractory would solve all problems if only it were more readily obtainable. Such hopes seem born to wilt under examination of each of the refractories in question. A fairly recent survey by Birch [20] of the refractories available for use above 1800° c. led to the conclusion that alumina, magnesia and zircon (and carbon) were the only practicable propositions.

In furnace operation it is worth pointing out that when the overall cost of installation and operation is considered, there is not much to choose between platinum alloy windings and molybdenum. Furthermore the high initial cost of platinum is offset by its recovery value. The chief disadvantage of platinum alloys as against molybdenum is that the former cannot economically be used above about 1500° c., whereas the latter is only limited by the refractory tubes available.

Dr. J. White (*Sheffield*) said : In connection with the paper by Dr. Kitchener and Dr. Bockris, I used molybdenum-wound furnaces in Glasgow from 1931 onwards. The first furnaces had been constructed by Prof. Higgins some years earlier, and the technique used was inherited from him. Each worker made his own refractory tubes from alundum cement and wound them himself. Our furnaces were certainly not treated with the excessive care described by the authors. Normally we took about one and a half hours to reach 600° c. from cold, otherwise we tended to get explosions on reaching the ignition range of hydrogen-air mixtures (possibly due to the presence of pockets of air which had not been swept out). Thereafter the current was kept at its maximum safe value—about 30 amp. with our windings—enabling us to reach 1600° c. in about 3 hr. from starting. No special precautions were taken during the first heating of a new furnace. Failures due to the refractory rarely if ever occurred, and I have known windings to last over a year in fairly continuous use. Our maximum temperatures were, however, rather lower than that quoted by the authors being generally of the order of 1650° c. though on occasions we exceeded 1750° c.

The construction of our furnaces differed slightly from that described by the authors in that we placed a second alundum tube of wider diameter around the actual furnace tube. This kept the insulating material from the furnace tube and provided an annular space into which the incoming gas (cracked ammonia) was led so that it passed directly over the winding. With this arrangement there would appear to be less chance of oxidation of the winding due to retention of air or moisture by the insulation. There is, of course, some sacrifice of insulation and we used to compensate for this to some extent by covering the winding with a fairly thick layer of alundum cement.

One other point in connection with the use of these furnaces should, I think, be mentioned, namely, that the resistance of the winding increases some seven times between room temperature and 1600° c. It is, therefore, necessary to start with a low voltage across the winding and to increase this progressively as the temperature rises.

Regarding the use of platinum-base thermocouples or windings, as mentioned by the authors, these will pick up silicon in a reducing atmosphere if they are in contact with refractories containing silica. What is perhaps not so well known is that even small amounts of sulphur in a reducing atmosphere will cause platinum to pick up silicon from siliceous refractories not in direct contact with it due to formation of volatile sulphides of silicon.[21] The mechanism is apparently similar to that by which the pick-up of silicon by liquid iron described by Skelly and myself occurred. A low-melting platinum-silicon alloy is formed. In an industrial application, I have known platinum thermocouples to melt at temperatures below 1450° c. due to this cause after cracking of the refractory sheath. In the laboratory I once had it occur due apparently to volatilisation of sulphur from rubber bungs which had been allowed to become rather hot.

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[20] *Ohio State Univ. Eng. Expt. Station News*, 1945, **17**, (4)3.

[21] *J. Iron Steel Inst.*, 1947, **155**, 213.

With regard to the paper by Mr. Dastur and Prof. Chipman, I have never been quite clear as to why the use of a preheater in the manner described for the prevention of thermal diffusion should also have been effective in preventing sulphur deposition from H_2–H_2S mixtures as described by Chipman and Ta Li [22]. Skelly and I always got sulphur loss when we used a wide reaction tube with cold ends, even when we introduced the gas directly to the hot zone by lengthening the inlet tube. We overcame this trouble by using a relatively small reaction chamber placed entirely in the hot zone of the furnace, and by using narrow inlet and outlet tubes so that the gas entered and left the chamber at a relatively high velocity. Only then did we get good agreement between the analyses of the ingoing and outgoing gases.

Mr. J. H. E. Jeffes (*B.I.S.R.A., London*) (*communicated*): I should like to add one or two points to the paper of Kitchener and Bockris which are possibly of interest to workers in this field. The carbon tube resistance furnace is not really open to all the criticism levelled against it here. In practice the same kind of protection from oxidation as is used for molybdenum can be employed, and a uniform temperature zone can be closely approximated by judicious shaping of the walls of the tube, so that they have a greater resistance per unit length at the ends than in the middle. This is precisely analogous to the common practice of winding resistance elements more closely at the ends than in the middle, in order to counteract end-losses. The most serious actual disadvantage is the heavy amperage usually needed by these furnaces.

In the section on temperature measurement, no mention is made of resistance thermometers. Since the automatic control of furnace temperatures above 1600° c. is very desirable, some preliminary experiments have been made in the B.I.S.R.A. Chemistry Laboratories on the use of a molybdenum resistance wire for this purpose. The high-temperature coefficient of resistance of molybdenum lends itself to this purpose, and a valuable safeguard against overheating exists in that any corrosion of the element, or discontinuity in its electrical circuit will result in a *lowering* of the furnace temperature under the action of a controller, whereas a thermocouple-controlled furnace will always tend to run away when the thermocouple is contaminated or its circuit broken. This thermometer could be adapted as an absolute instrument by attaching two leads to each end of the element and measuring the lead resistance at high temperatures by combination. A molybdenum resistance thermometer could be electrically annealed in hydrogen just below its melting point in a manner analogous to that described by Chipman for tungsten-molybdenum thermocouples.

Lastly, I believe that a new type of base metal resistance heating element has recently become available in this country. It is coated with a layer of aluminium metal which oxidises to a coherent film of alumina on heating, and enables the element to be run in air for long periods at 1350° c., at which temperature any normal base metal element would be rapidly oxidised.

Dr. J. O'M. Bockris (*London*) (*partly communicated*): We thank Mr. Barrett for pointing out that our paper gave the impression that BN might be a general panacea to refractory troubles. No such impression was intended. However, it is worth mentioning that it is unattacked [23] by molten Fe_3O_4 and has been produced commercially. The examination of the refractory properties of other nitrides seems desirable, e.g., silicon nitride. If availability is taken into account, then only three refractories need be considered at present for temperatures above 1800° c., fused alumina, magnesia and zircon. A considerable number of substances have softening points above 2000° c. and the following may be mentioned as potential refractories with softening or decomposition temperature above 2500° c.: beryllia, zirconia, hafnia, thoria, nitrides and carbides of titanium, tantalum and zirconium and some borides of the transition elements.

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[22] *Trans. Amer. Soc. Met.*, 1937, 25, 435.

[23] Mellor, *Inorganic and Theoretical Chemistry* (London, 1928), Vol. VIII, p. 111.

The long time given for running-in the alumina tubes of the authors' molybdenum furnaces is a result of experiences gained using a shorter time. It must be pointed out that authors who claim this initial treatment of the tube is unnecessary usually do not use their tubes above 1650° c., whereas the tubes referred to by the present author are brought regularly to 1800° c.

It is comparatively easy to deal with the deterioration of alumina when it is used up to temperature of only 1650° c., a contention supported by the fact that alumina tubes suitable for this temperature can easily be made in the laboratory, whereas the manufacture of satisfactory alumina tubes for use at 1800° c. is a difficult task. The essential points in the long running-in period are the elimination of water, the slow expansion of the alumina which is about 0·9 % over the range 0–1800° c. and the corresponding sintering process for tubes of Morgan's Triangle R Brand.

In view of the remarks of Dr. White and Mr. Barrett concerning the "excessive care" with which the present author and his colleagues treat their furnaces, it is noteworthy that refractory and furnace manufacturers recommend 100 hr. for running-in rather than the 80-90 hr. used by the author for Morgan's Triangle R alumina tubes.

Regarding Mr. Barrett's remarks concerning controlled atmospheres and suitable impervious inner tubes for these, fused alumina is very satisfactory up to at least 1800° c.; fused beryllia may also be of use here. Zircon tubes, though permeable to hydrogen, are more economical to use for inner tubes when a small amount of diffusion is of no account. More attention should be paid to micronised zircon as a very useful general refractory resistant to many acid (non-ferrous) slags; it is stable to 1900° c. in hydrogen and to 2400° c. in an oxidising atmosphere. It cannot, unfortunately, be used as a furnace tube for resistance wire owing to the high electrical conductivity

The ideal of those interested in the construction of electrical resistance furnaces is to be able to produce a temperature of 2500° c. in air and it seems profitable to pursue research in this direction with the aid of zircon tubes, which have a comparatively high electrical conductivity and which, therefore, could be used as the heating resistors. It remains to devise a satisfactory arrangement for the initial heating of this tube to a temperature at which sufficient conduction for heating purposes occurs.

The author has successfully used nitrogen-hydrogen mixtures of high nitrogen content as atmospheres in molybdenum resistance furnaces. Apart from the diminution of reducing properties, compared with hydrogen, these mixtures have the advantage of being non-explosive. The furnace is flushed with pure hydrogen after the measurements are completed to reduce any molybdenum oxides formed. In connection with oxide formation, it is necessary to eliminate from the furnace, water, which otherwise attacks molybdenum to form the volatile oxide MoO_3. Two conditions reduce the water content in the furnace: (i) the use of calcined alumina of coarse grain size (sandy in appearance) in the insulating powder of the furnace; any caking of the alumina powder indicates the presence of an undesirably high water content; (ii) a long heating-up period before carrying out measurements, particularly in the period following upon the introduction of a new furnace tube, when the cement contains much excess water.

We agree with the remarks of Mr. Hopkins on induction furnaces. What we wished to underline in our paper was that (*a*) molybdenum and tungsten resistance wire furnaces were suitable and efficient for many purposes up to about 2000° c.; and therefore that in view of the considerable difference in cost were generally preferable to induction furnaces except in cases where these *must* be used; (*b*) in some experiments the rapid rate of heating and cooling which is often a characteristic of an induction furnace and in many types, the difficulty of satisfactory temperature control was undesirable.

Dr. Kubaschewski's remarks on the evaporation of an *oxide* of platinum clarifies a point which we should have made more clearly in our paper. The oxide is unstable and decomposes on cold parts of the furnace to yield platinum.

Whether this evaporation is considered *dangerous* at 1500° c., however, clearly depends on the thickness of the winding and the value of platinum. With commercial types, lives of 200–1000 hr. (depending on the thickness of the winding) at a temperature of 1250°–1500° c. in air are usual and this seems satisfactory enough.*

With regard to Pt in SiO_2, we can support Dr. White's remarks ; in a reducing atmosphere we have found that platinum electrodes which we attempted to use for conductivity measurements formed with silicon an alloy which melted at about 1400° c.

The problem of a refractory resistant to molten FeO is still unsolved. A number of measurements can be carried out in Fe crucibles, which are usable up to about 1400° c., a sufficient temperature, for example, for a fairly extensive examination of the system $FeO–SiO_2$.[24] [25] The principal property needed in a refractory for FeO is, in addition to the absence of a eutectic with FeO, a low rate of diffusion into the refractory. MgO, one of the most likely choices, is fairly rapidly attacked, and can only be used for some types of experiments in induction furnaces, where the time during which the melt is at high temperatures is very short.[26] The potentialities of fused refractory materials in resisting FeO does not seem to have been investigated systematically.[27] If they are found unsuitable it may be necessary to resort to more novel means, e.g., to attempt some arrangement in which a "cup" of molten FeO is formed in a block of externally cooled solid FeO by arc or infra-red heating. Molten Fe seems a probable electrode material.

Dr. F. D. Richardson (*B.I.S.R.A., London*) said : I feel it important that besides quoting the dimensions of their inlet preheating tube, Mr. Dastur and Prof. Chipman should report either the minimum flow-rate at which they found no diffusion error, or the minimum rate they actually employed in getting reproducible results. Their system of adequately preheating the gas does not necessarily eliminate the thermal diffusion error, it merely transfers the expected upper concentration gradient in the apparatus to a point nearer the gas inlet. The concentrations of hydrogen and water vapour at the crucible will only be equal to the ingoing and outgoing concentrations, if the flow rate is too fast to allow any significant concentration gradient to be built up and maintained. It is hardly necessary to summarise the reasons for this view since Darken and Gurry [28] have already analysed the problem of thermal diffusion in a vertical furnace tube under steady conditions, where the inlet and outlet gas mixtures have the same composition.

Mr. J. H. E. Jeffes (*B.I.S.R.A., London*) (*communicated*) : I would like to suggest, as a slight further development of this excellent preheating technique, that a cross-piece of platinum wire stretched across the bottom of the preheater tube would provide a rapid method of checking the gas temperature, since, when viewed through an optical pyrometer, this cross would disappear against the liquid metal background when the gas was at the same temperature. This would enable the preheater current to be easily adjusted to its best value.

When they were making experiments near to the saturation value of oxygen in liquid iron it is presumed that the authors may have experienced some attack of their alundum crucibles by liquid FeO. This point has also been raised by Kitchener and Bockris in their paper on practical methods of investigating high-temperature reactions, where they mention the difficulties of avoiding attack on refractories when dealing with slags with a high FeO content. This problem was very elegantly avoided by Taylor and Chipman in their researches on the liquid iron-liquid iron oxide system in 1942, by the use of a rotating crucible. More recently, attempts to use this technique with more complex slags have been made in Britain, with little success.

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[24] Wejnarth, *Trans. Electrochem. Soc.*, 1934, **65** (preprint); *Trans. Electrochem. Soc.*, 1934, **66** (preprint).

[25] Darkin and Gurry, *J. Amer. Chem. Soc.*, 1945, **67**, 1398.

[26] Hay (private communication).

[27] Tritten and Hansen, *J. Iron Steel Inst.*, 1924, **110**, 90.

[28] Darken and Gurry, *J. Amer. Chem. Soc.*, 1945, **67**, 1411.

* Johnson Matthey (private communication).

In an attempt to discover the reasons for these failures, we have studied the question of the forces acting on such a rotating system, and have performed experiments on pairs of immiscible liquids rotating in the cold. Briefly, the results of these experiments are that such a system conforms to the theoretical requirement that the shapes of the surface paraboloids are independent of the liquids, except where surface tension affects them. It was found possible to form a stable pool of " slag " on the surface of the " metal " and not touching the sides of the vessel, when the inter-liquid surface tension was high and the amount of " slag " did not quite cover the whole surface of the " metal " when the system was not rotating. This may explain why Taylor and Chipman were successful with a pure FeO slag, which would appear to exhibit a high surface tension with respect to liquid iron.

Apart from this surface tension effect, which operated only at the edges of the " slag " layer, the " slag " film appeared to be perfectly uniform in thickness, and we suggest that the contrary effect noted by Taylor and Chipman on a melt cooled whilst rotating may have been due to the change in the shape of the metal surface which occurred when the induction power was shut off.

It has been found, however, that a deep and stable pool of " slag " could be formed in the centre of the " metal " in the systems studied (water-carbon tetrachloride and mercury-acetylene tetrabromide) when the " slag " layer was prevented from rotating as fast as the " metal " by means of brake, either in the form of a solid shape dipping in the " slag " only, or by a tangential gas jet playing on the " slag " layer in a direction opposed to its rotation.

We hope that this last technique may prove useful in investigations in this field.

II. ROASTING AND REDUCTION PROCESSES

ROASTING AND REDUCTION PROCESSES—A GENERAL SURVEY

By C. W. Dannatt and H. J. T. Ellingham

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Metallurgy, one of the most ancient arts, originated with the use of particles of native metal as ornaments and with their fabrication into primitive implements and utensils.[1] These uses of metals belong to the Stone Age for the metal was a " pebble " shaped by hammering. Metallurgy proper, and the recognition of metals as such, commenced with the advent of primitive melting and smelting, operations that presumably originated with the reduction of those lumps of ore which, by chance, formed part of the ring of stones enclosing the domestic fire.[2] The development of pyrometallurgy from such simple beginnings was due in the early days to chance discoveries and in later times, after a lapse of some 2000 years during which little or no advance was made,[3] to experimentation by trial and error. The remarkable progress achieved in the latter period is a tribute to the energy and resourcefulness of the early metallurgists, but as extraction metallurgy is, in the main, applied physical chemistry, future developments must be based upon the co-ordinated work of the pure scientist and the applied scientist, of the physical chemist and the metallurgist. The metallurgist must be trained to understand and utilise the fundamental information provided and to present his problems in a suitably explicit form. The physical chemist, on the other hand, should have sufficient knowledge of plant requirements so that his answer may be readily translated into practice. The value of such team-work is gaining ever wider appreciation and holds promise of a rich reward.

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[1] Rickard, *Man and Metals*, 1932, 1, 91 *et seq.*

[2] Gowland, *J Inst. Metals*, 1912, 7, 24.

[3] Carpenter, *Metals in the Service of Human Life and Industry* (Brit. Sc. Guild, Annual Research and Development Lecture, 1933).

Occurrence of Metal-bearing Minerals: Stages in the Extraction of Metals

A few of the less reactive metals occur in nature in the metallic state Most of the gold obtained, and notable proportions of the platinum metals, are derived from deposits containing these native particles, while useful amounts of silver, copper and a few other metals have been obtained from similar sources. Apart from such occurrences, however, all the metals normally are found as minerals consisting of compounds such as oxides, sulphides, carbonates, silicates, etc Sometimes the mineral is a relatively pure, simple compound of a single metal, but more often it is complex and is composed of a number of elements, some of which may replace others in varying proportions. In any event, the extraction of metals from their ores necessarily involves a series of concentrations, or separations, even though the required or permissible product is an alloy Separation is effected by the utilisation of physical properties such as density, fusibility, volatility and the like, and chemical treatments are applied for the production of compounds or the liberation of elements that possess such distinctive characteristics as can be employed for this purpose.

Most metal-bearing minerals, including native metals, commonly occur, not as massive deposits, but disseminated, coarsely or finely, through a mass of rock After grinding to liberate the mineral, the latter can usually be concentrated by some simple mechanical means. Selective flotation, which takes advantage of surface phenomena, is now the most important of these operations and is commonly employed where two or more metals are associated together in the ore. This frequently happens with the sulphides of lead, zinc and copper. Oxidised materials are seldom amenable to such treatments but may sometimes be subjected to direct chemical attack by lixiviants.

When no further concentration can be effected by such means, chemical action must be employed to produce new compounds which can then be separated by the use of similar methods, such as separation by gravitational flow at elevated temperature, possibly after chemical reduction of the metal. Subsequent operations then follow along similar lines until a product of sufficient purity is obtained.

In many instances the metal-bearing mineral is not a substance from which the metal is readily or economically separable by a direct reduction process and it may then be necessary to convert it into some other compound by a preliminary chemical treatment. Thus, carbonates are commonly converted to oxides by calcination and sulphides wholly or partly to oxides by roasting. Sulphides may also be partly converted to sulphates by roasting under carefully controlled conditions, or to chlorides by chloridising roasting, and in some cases it may be desirable to convert oxides to sulphates by treatment with sulphuric acid.

The selection of such processes and the conditions of their operation depend upon a variety of factors. The major difficulty is the complexity of the material under treatment. A particular type of reduction process may be preferred because it is best suited to follow preliminary operations that give the most effective separation from other constituents present, or because it is itself adapted to the elimination of impurities, thereby simplifying or rendering unnecessary a subsequent refining process. If one or more of the substances to be removed is of sufficient value, the extent to which it can be recovered at any stage may have a determining influence on the procedure to be adopted.

It is necessary, therefore, to consider the various stages of an extraction process as parts of a whole, for a modification of any one stage, by changing the nature or extent of the separations it effects, may require or permit changes of procedure in the other stages, or may even allow some of them to be omitted. The position may also be affected by the purity required in the metal, for this may vary greatly according to the purpose for which it is to be used. A demand for a particular metal in a higher state of purity than is normally required, perhaps in respect of freedom from specific impurities, may make it desirable to adopt an extraction process entirely different from that usually employed. For example, the demand for high-purity zinc in the production of cartridge brass in the 1914–18 war resulted in the rapid development, alongside the customary pyro-metallurgical process, of a hydro-metallurgical process, involving electrodeposition of zinc from sulphate solutions obtained by leaching roasted concentrates with sulphuric acid solutions.

On the other hand, where a metal is to be used as an alloying element, it may not be necessary to extract it as such if, by a simpler or more economic reduction process, it can be obtained as a "master alloy" with the metal into which it is to be introduced. For example, steel-alloying elements such as manganese and titanium, are commonly produced for this purpose as ferro-alloys, while beryllium, which is particularly difficult to obtain in the elementary state, is mainly produced as a rich alloy with copper from which useful copper alloys with low beryllium content are readily obtained.

Applications of Free-energy Data

Subject to these considerations, the primary aims in the extraction of a given metal from a particular ore or concentrate are to minimise the number of separate processes involved and to ensure that each shall give, at a reasonable rate of operation, the highest overall efficiency in the recovery of the metal and any valuable by-products, with the minimum of expenditure on other materials (fuels, fluxes, leaching agents, etc.), on energy (thermal or electrical) and on other operational and maintenance costs.

Pyro-metallurgical processes require the use of elevated temperatures but it is essential that the temperature shall be kept as low as possible consistent with the occurrence of the desired reactions at an adequate rate and with a satisfactory degree of separation. As the working temperature is raised, the capital cost of plant and the operational and maintenance charges increase rapidly, especially when the temperature exceeds that which can be readily attained by the combustion of ordinary fuels. Again, operation at reduced pressures entails increased expenditure on plant and is not undertaken unless there are compensating advantages. This would be still more true for processes at pressures substantially greater than atmospheric, but these have not so far been introduced into metallurgical practice. Nevertheless, improvements in materials of construction and in techniques have led to the economic operation of processes requiring progressively higher temperatures and, to some extent, low pressures, where available alternative methods are abnormally costly or less efficient. New possibilities of recovering and refining metals by vaporisation have thus been developed.

As a first means of assessing the practicability of possible chemical processes in the extraction of metals, data for the free-energy changes accompanying them at various temperatures and pressures are of obvious importance, for the higher the free energy of a reaction under specified conditions the greater is its tendency to occur under those conditions. In recent years such data, previously widely scattered in the literature, have been collected, correlated and expressed in the form of equations relating standard free energies of formation with temperature, for compounds of major metallurgical interest, such as oxides (by Thompson [4]), carbonates, sulphides and sulphates, carbides and nitrides (by Kelley and his collaborators [5]). Much remains to be done in improving the accuracy of such data, especially in the higher ranges of temperature, and in extending them to cover other classes of compounds, but the figures already available serve to give at least an approximate basis for many investigations.

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[4] *The Total and Free Energies of Formation of the Oxides of Thirty-two Metals* (The Electrochemical Society, 1942).

[5] *U.S. Bur. Mines Bull.*, **384**, 1935; **406**, 1937; **407**, 1937.

It has been shown by Ellingham [6] that the chart obtained by plotting against temperature the standard free energy of formation ($-\Delta G^\circ$) of compounds of a particular class (say oxides) of the various chemical elements, by indicating the relative oxidisabilities of those elements and the relative reducibilities of their compounds, exhibits directly the conditions under which such reactions tend to occur and the possibility of effecting separations by taking advantage of the differences in these tendencies. The chart for sulphides is reproduced here (Fig. 2), together with a revised chart for oxides (Fig. 1). The authors are indebted to Dr. F. D. Richardson and Mr. J. E. H. Jeffes for making available data for certain oxides derived from their recent critical examination of the relevant literature in connection with a paper they are about to publish.

An alternative system of representation for oxides has been independently developed by Pourbaix,[7] in which the logarithm of the equilibrium oxygen pressure (which is directly proportional to the standard free energy of formation divided by the absolute temperature) is plotted on the reciprocal of the absolute temperature. The significance of diagrams of this type in the study of metallurgical equilibria and processes is discussed in a paper by Pourbaix and Rorive-Bouté.[8]

Free-energy data for chemical reactions are commonly obtained from thermal measurements, involving determinations of heat of reaction and entropy change, the latter generally entailing measurements of specific heats and latent heats of change of state for the participating substances over a wide range of temperature. In some cases direct measurement of an equilibrium constant is practicable and, for the formation of a simple compound, may entail only the determination of the partial pressure of one or more gaseous participants. Examples of special techniques in the application of this method to the study of novel processes are described in papers by Gross, Campbell, Levi and Kent (the reaction $2Al + AlCl_3 = 3AlCl$)[9] and by Gross and Mrs. Warrington (the reaction $ZnS(s) + Fe = FeS + Zn(g)$).[10] In view of the simple relation between the free energy of formation of a substance and its decomposition voltage or the E.M.F. of the corresponding voltaic cell (cf. Fig. 1 and 2), these electrochemical measurements may also be employed. Indications of the scope of such methods at elevated temperatures using molten salt electrolytes are given in the paper by Rose, Davis and Ellingham.[11]

In Fig. 1 and 2 the free energy of formation in kcal./g. mol. oxygen or sulphur is plotted downwards and a parallel scale in volts (representing decomposition voltage) has been added. A pressure-correction chart serves to show the extent of the change due to any gaseous participant being at a partial pressure greater or less than 1 atm. The lower the position of a line on the oxide diagram the greater is the affinity of the element for oxygen at 1 atm. pressure and the smaller the oxygen dissociation pressure of the oxide (or higher oxide). At a given temperature the vertical distance between two lines shows the tendency of the reaction represented by the lower line to drive backwards that represented by the upper line, i.e., for the element concerned in the former to displace that in the latter from its oxide. Similar relations are shown by the sulphide diagram. The conditions of temperature and pressure under which an oxide or sulphide tends to be reduced by some other element (or other oxide or sulphide) can be read off directly from the appropriate diagram. Moreover, the conditions for the occurrence of such reactions as

$$MS + 2MO = 3M + SO_2,$$

$$\text{or } 2MS + 3O_2 = 2MO + 2SO_2$$

are readily deduced by the use of both diagrams.

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[6] *J. Soc. Chem. Ind.*, 1944, **63**, 125.

[7] *Bull. Soc. chim. Belg.*, 1944, **53**, 145; *Rev. Métall.*, 1947, **292**; *Complex Chemical Equilibria: Method of Calculation and Graphical Representation* (Ed. Science et Technique, Brussels, 1948).

[8] This Discussion.

[9] This Discussion.

[10] This Discussion.

[11] This Discussion.

These two diagrams thus provide a conspectus of metallurgical possibilities in respect of oxidation and reduction processes in which metals, their oxides and/or their sulphides are concerned. Similar diagrams for other classes of compounds, such as carbides and silicates, are needed. Also, since the diagrams refer to solid or liquid participants at unit activity—as separate pure phases or as saturated solutions—more information is required on the activities of such substances as unsaturated solutions in particular systems, for it cannot be assumed that such activities are even approximately represented by concentrations.

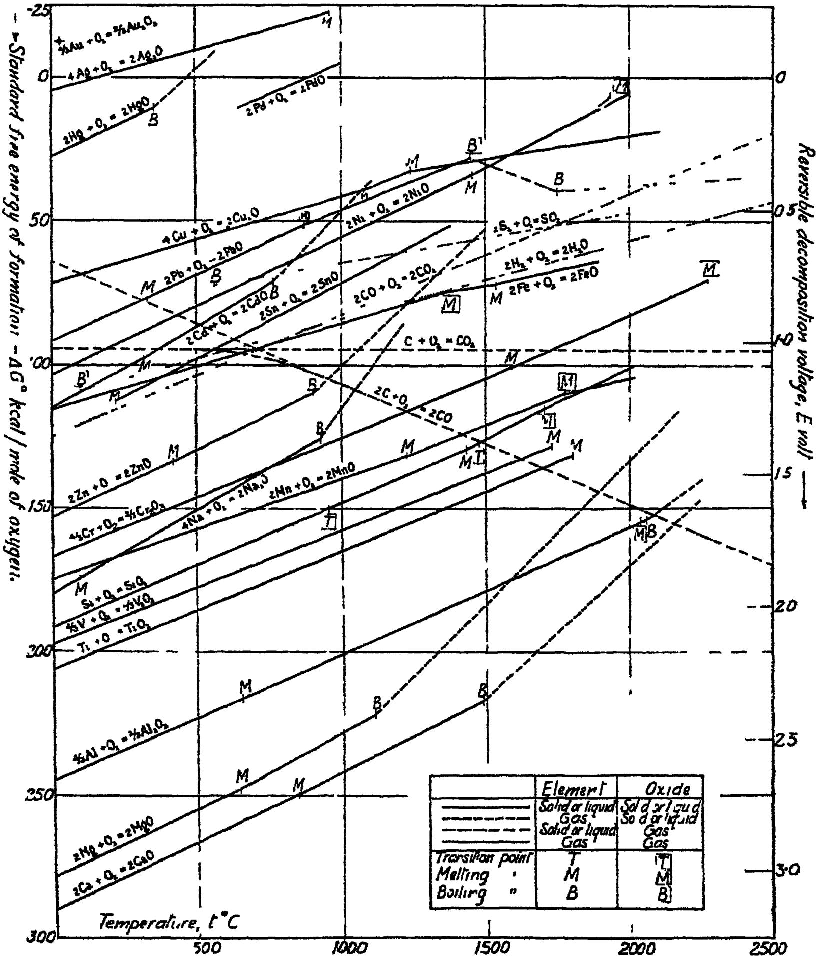

FIG. 1.—Standard free energy of formation (− Δ G°) of oxides: variation with temperature.

Mechanism and Rate of Reactions in Extraction Processes

The standard free energy of a reaction at a given temperature is a measure of its tendency to occur under those conditions when all the participating substances are at unit activity. In a closed system the consumption of reactants and formation of products of variable activity (substances in the gaseous state or in unsaturated solutions) leads to a progressive decrease in the free energy, which would become zero at equilibrium. Although at the temperatures used in pyro-metallurgical practice a positive tendency for a reaction to occur generally means that it does, in fact, take place at an appreciable rate, the magnitude of the free energy for the reaction as a whole at any stage affords no indication of the rate of occurrence under those conditions, though the velocity must, of course, tend towards zero as equilibrium is approached. Reaction velocities must, therefore, be the subject of independent study, and any calculation of their magnitude requires a knowledge of the mechanism of the reactions concerned.

The reactions involved in roasting and reduction processes are largely heterogeneous, occurring at solid-liquid, liquid-liquid, solid-gas or liquid-gas interfaces.

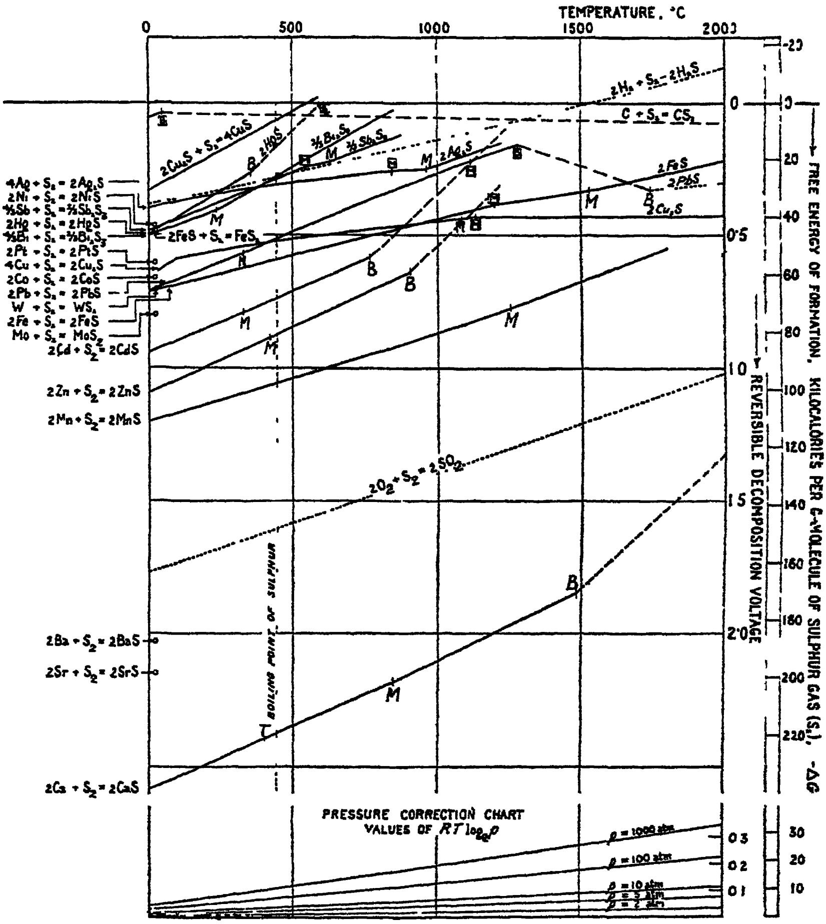

FIG. 2.—Standard free energy of formation ($-\Delta G^\circ$) of sulphides: variation with temperature.
Chart embodying data published prior to 1942.
Reprinted from *Trans. Soc. Chem. Ind.*, 1944, **63**, 125–133.

Reactions between solids are relatively insignificant, and reactions that appear to belong to this category probably proceed by way of a gas phase. Thus, in the reduction of solid oxides by means of carbon there is no doubt that the effective reducing agent is carbon monoxide ($MO + CO = M + CO_2$), but as the partial pressure of the resulting CO_2 is being continuously prevented from rising by the reaction $CO_2 + C = 2CO$, whereby CO is re-formed, the thermodynamic relations for the process correspond to reduction by carbon with formation of the equilibrium $CO—CO_2$ mixture at the given temperature, whereas the rate of reduction will depend on the velocities of the gas-solid reactions involved. In Fig. 1, a curve is given for the free energy of oxidation of carbon to the equilibrium CO–CO_2 mixture, which at lower temperatures (below about 600° c.) merges into that for $C + O_2 = CO_2$ and at higher temperatures (above about 900° c.) into that for $2C + O_2 = 2CO$. This composite curve would indicate the effective reducing tendency of carbon at any temperature if the partial pressure of CO_2 were continuously kept down to the equilibrium value by reaction with carbon—a condition that may never be completely realised in practice.

The paper by Juliard, Rayet and Ludet[12] shows that the dissociation of carbon monoxide, $2CO = C + CO_2$, the reverse of the above reaction, not only requires for its occurrence a catalyst such as iron or nickel, but also that the metal should be associated with the corresponding oxide or with graphite as a promoter.

For reactions occurring at an interface between two phases, the rates at which reactants can be brought to the interface and products removed from it often determine the velocity of the reaction as a whole. In such cases the reaction velocity may be increased by movement of the fluid phase or phases, e.g., by causing a liquid or gaseous reactant to flow across the surface of a solid reactant. In such processes, however rapid the streaming, there will always be a stationary fluid film in contact with the solid, through which the transport of reactants and products must be maintained by diffusion, and, in reactions between a gas and a porous solid, diffusion through the gas-filled pores may also intervene between the gas stream and the inner solid surfaces at which the reaction mainly occurs. In the paper by Woods[13] a critical examination of the results of experimental investigations of the reduction of oxides of iron by carbon monoxide or hydrogen leads to the conclusion that the velocity of reduction is essentially determined by rates of diffusion through such gas films.

If in a gas-solid reaction there is a gaseous product as well as a gaseous reactant, the continuous removal of the former from the sphere of action in a gas stream may have an important effect on the velocity of the whole process, for the partial pressure of the gaseous product at the surface of the solid may be kept down to an extremely low value. By this means, reactions that would be thermodynamically impossible with the gaseous participants at atmospheric pressure may be caused to proceed rapidly. Thus in a stream of hydrogen, oxides with a much greater standard free energy of formation than steam at 1 atm. pressure may be effectively reduced at suitable temperatures; even an oxide as stable as MnO can be reduced in this way.

Under the conditions of occurrence of most pyro-metallurgical processes it seems that the intrinsic rate of a heterogeneous reaction would have to be unusually low for diffusion to cease to be the controlling factor. In his introductory paper, Sir Charles Goodeve has discussed the dependence on temperature of the magnitudes of these intrinsic reaction rates in relation to activation energies and this aspect of the subject need not be further considered here. Reference must be made, however, to the discussion by Anderson[14] of the detailed mechanism of reactions of the type:

$$\text{solid (A)} + \text{gas (B)} = \text{solid (C)} + \text{gas (D)},$$

in relation to lattice defects; the mechanisms proposed for such primary reactions in roasting and reduction processes are supported by experimental determinations of changes in semi-conducting properties of oxides and sulphides.

Extraction Processes in Metallurgical Practice

In Table I the chemical elements are arranged in the form of a periodic table with special reference to characteristics of the metals relevant to their extraction. Dotted lines are employed to separate the metals from the non-metals and to demarcate respectively the noble metals (those most readily obtained by reduction of their compounds) and the highly reactive metals (those most difficult to obtain by reduction). Broken lines serve to indicate metals that have exceptionally low boiling points (below 1200° c.) and are thus most readily recovered by distillation. Full lines are employed to show the metals with relatively low melting points (below 450° c.) and with relatively high melting points (above 1500° c. and above 1900° c.); the former are easy to obtain by smelting, whereas the production of the latter, especially those melting above 1900° c. may entail special processes, e.g., electrothermal operations. Other characteristics of individual metals are indicated by the following conventions :—

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[12] This Discussion.
[13] This Discussion.
[14] This Discussion.

(*a*) Metals whose extraction is of major (minor) metallurgical importance—symbol surrounded by a full circle (broken circle).

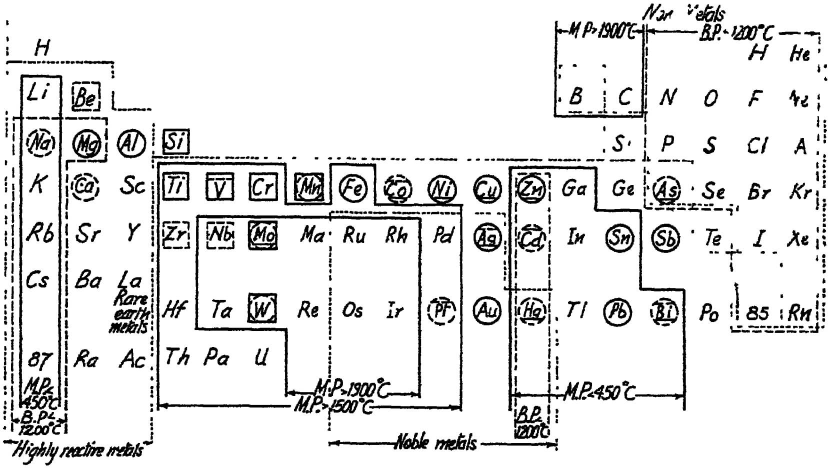

TABLE I

PERIODIC TABLE INDICATING SOME OF THE CHARACTERISTICS OF THE METALS RELEVANT TO THEIR EXTRACTION

(X) METAL WHOSE EXTRACTION IS OF MAJOR METALLURGICAL IMPORTANCE

(X) METAL WHOSE EXTRACTION IS OF MINOR METALLURGICAL IMPORTANCE

$\boxed{X}$ METAL WHOSE EXTRACTION IN THE FORM OF AN ALLOY WITH SUBSTANTIAL PROPORTIONS OF ANOTHER METAL IS OF MAJOR IMPORTANCE

$\boxed{X}$ METAL WHOSE EXTRACTION IN THE FORM OF AN ALLOY WITH SUBSTANTIAL PROPORTIONS OF ANOTHER METAL IS OF MINOR IMPORTANCE

$\underline{X}$ METAL WHICH IS EXTRACTED TO A LARGE EXTENT FROM NON OXIDISED ORES

$\overline{X}$ METAL WHICH IS OBTAINED ENTIRELY OR MAINLY IN THE COURSE OF EXTRACTION OF ANOTHER METAL

$\overline{X}$ METAL WHICH IS OBTAINED TO A NOTABLE EXTENT IN THE COURSE OF EXTRACTION OF ANOTHER METAL

(*b*) Metals whose extraction in the form of an alloy with substantial proportions of another metal is of major (minor) metallurgical importance—symbol surrounded by a square (broken square).

(*c*) Metals which are extracted to a large extent from unoxidised ores (e.g., from sulphides or arsenides)—symbol underlined. This distinction is of importance as extraction from unoxidised ores generally entails some form of chemical treatment (e.g., roasting) prior to reduction to metal (see below).

(*d*) Metals which are obtained entirely or mainly (to a notable extent) in the course of extraction of another metal—full line (broken line) above the symbol.

(*e*) Symbols without any of the above signs refer either to non-metals or to metals whose extraction is of very little metallurgical significance although the metals may be of value in special applications.

All the above-mentioned characteristics may influence the nature and conditions of operation of the extraction process and, if account be taken also of the importance, already emphasised, of removing at each stage other elements derived from the ore, it should be possible to provide a rational basis for the varied schemes adopted in practice. A general survey of typical processes in extraction metallurgy is given in Table II. In this table, reference is made to hydro-metallurgical as well as pyro-metallurgical processes in order to provide a general picture of the scope of current practice.

TABLE II—TYPICAL PROCESSES IN EXTRACTION METALLURGY

Metal	Starting Material	Preliminary Treatments	Reduction to Metal	Purification Treatments	Metallic By-products
Aluminium ..	Oxide Ore	Chemical Separation (Al_2O_3)	Electrolysis from Fused Bath	Thermo-electrolysis	—
Antimony ..	Sulphide Ore	Liquation (Sb_2S_3)	Iron Reduction	Slag Refining	Ag, As, Au
	Sulphide and Oxidised Ores	Roasting (Sb_2O_4) Volatilising Roasting (Sb_2O_3)	Carbon Reduction	Slag Refining	
Arsenic ..	Sulphide Ore or Concentrates	—	Distillation (As)	Redistillation	Ag, Au, Sb
	Sulphide Ore, Concentrates, Fume, Residues, etc.	Volatilising Roasting (As_2O_3)	—	Redistillation (As_2O_3)	
Beryllium ..	Oxide Ore	Chemical Separation (BeF_2)	Magnesium Reduction (Be-Cu) Electrolysis from Fused Bath (Be-Cu)	—	—
		Chemical Separation (BeO)	Carbon Reduction in Electric Furnace (Be-Cu)	—	
Bismuth ..	Sulphide Ores Flue Dust, etc.	Roasting Chemical Separation (BiOCl)	Carbon Reduction	Slag Refining	Ag, Au, Cu, Pb
Cadmium ..	Spelter	—	—	Fractional Distillation	—
	Blue Powder	—	Carbon Reduction and Volatilisation	Redistillation	
	Flue Dust, Fume, etc.	Chemical Purification	Electrolysis Chemical Precipitation	— —	
Calcium ..	Carbonate Ore	Chemical Separation ($CaCl_2$)	Electrolysis from Fused Bath	—	—
Chromium ..	Concentrates	—	Ferro-silicon Reduction in Electric Furnace (Fe-Cr)	—	Pt Group
	Oxide Ore or Concentrates	Alkali Fusion; Chemical Separation (Cr_2O_3)	Aluminium Reduction Carbon Reduction	— —	
Cobalt	Sulphide Ores	Roasting; Matte Smelting; Roasting	Chemical Separation	Electrolysis (Co)	Ag, Au, Cu, Ni
	Arsenical Ores	Speise Smelting; Roasting		Ignition (Co_3O_4)	
	Oxidised Ores, Residues, etc.	Smelting to Complex Alloy		Crystallisation (Salts)	
Copper ..	Sulphide Ore or Concentrates	*Roasting; Matte Smelting*	Bessemerisation	Preferential Oxidation	Ag, As, Au, Cd, Co, Ni, Se, Te
	Oxidised Ores	Mix with Sulphides; Matte Smelting		Electrolysis	
	Low-grade Oxidised Ores	Lixiviation	Electrolysis Cementation on Iron	— Preferential Oxidation	
Gold	Free-milling Ores	Gravity Separation; Amalgamation; Distillation	—	Refining	Ag, Pt Group
		Cyanidation			
	Complex Ores	Flotation; Roasting; Cyanidation	Zinc Precipitation	Acid "Parting" Chlorine Refining Electrolysis	
	Electrolytic Slimes	Fusion and Casting Anodes	Electrolysis	—	
Iron	Oxide Ores Carbonate Ores Fines, Concentrates, etc.	— Calcination Sintering	Carbon Reduction	Foundry Iron Production Wrought Iron Manufacture Steel Making	—
Lead	Sulphide Concentrates, Oxidised Ores, Fume, etc.	Sintering	Carbon Reduction	Preferential Oxidation; Physical Separation Electrolysis	Ag, As, Au, Bi, Cd, Cu, Sb, Zn
	Antimonial Slags	—	Carbon Reduction (Sb-Pb)	—	

Magnesium ..	Carbonate Ore, Chloride Ore, Sea Water, etc.	Chemical Separation (MgO) Chemical Separation ($MgCl_2$)	Electrolysis from Fused Bath	—	—
	Dolomite	Calcination	Ferro-silicon Reduction under Vacuum	—	
Manganese ..	Oxide Ores	— Chemical Separation ($MnSO_4$)	Carbon Reduction (Fe-Mn) Electrolysis	— —	—
Mercury ..	Sulphide Ore	—	Distillation	Redistillation	—
Molybdenum ..	Sulphide Concentrates	— Alkali Fusion; Chemical Separation (MoO_3)	Carbon Reduction (Fe-Mo) Aluminium Reduction Hydrogen Reduction	— — —	
Nickel ..	Sulphide Concentrates	Roasting; Matte Smelting; Bessemerising to Ni_3S_2; Roasting	Carbon Reduction	Electrolysis	Ag, Au, Co, Cu, Pt Group
	Oxidised Ores	Smelting with Sulphides; Bessemerisation; Roasting	Hydrogen Reduction; Carbon Monoxide Volatilisation $Ni(CO)_4$; Decomposition	—	
Platinum ..	Alluvial Deposits	Gravity Concentration	Chemical Separation; Ignition of $(NH_4)_2PtCl_6$	—	Ag, Au, Ir, Os, Pd, Rh, Ru
	Electrolytic Slimes	—			
Selenium ..	Flue Dust, Fume, etc.	Roasting with Sulphuric Acid (SeO_2) Conversion to Sodium Selenite	Precipitation with Sulphurous Acid	Distillation	—
Silicon ..	Oxide Ore	—	Carbon Reduction in Electric Furnace (Fe-Si)	—	—
Silver ..	Ores	Amalgamation; Distillation Cyanidation Fuse with Unrefined Gold	— Zinc Precipitation "Parting"; Cementation on Iron	Inquartation and "Parting" Electrolysis	Au
	Doré Bullion	—	Electrolysis	—	
	Electrolytic Slimes	Fusion and Casting Anodes	—	Treat as Doré Bullion	
	Lead Bullion	Drossing; Softening; Zincing; Skimming; Distillation; Cupellation		Preferential Oxidation	
Sodium ..	Chloride Ore	Chemical Separation (NaCl)	Electrolysis from Fused Bath	—	—
Tin	Oxide Concentrates	Roasting; Leaching	Carbon Reduction	Physical Separation Preferential Oxidation	As, Bi, Cu, Nb, Sb, Ta, W
Titanium ..	Oxide Concentrates	Chemical Separation (TiO_2)	Aluminium Reduction	—	Ce, La, Nd, Pr, Th, Zr
Tungsten ..	Oxide Concentrates	Alkali Fusion; Chemical Separation (WO_3)	Carbon Reduction Hydrogen Reduction	— —	Nb, Sn, Ta
Vanadium ..	Oxide Concentrates	Alkali Fusion; Chemical Separation (V_2O_5)	Aluminium Reduction (Fe-V) Ferro-silicon Reduction (Fe-V)	— —	—
Tin	Sulphide Concentrates	Roasting and/or Sintering Sulphating Roasting; Lixiviation	Carbon Reduction and Volatilisation Electrolysis	Fractional Distillation Liquation —	As, Cd, Ge, In, Pb, Sb, Sn
	Fume, Residues, etc.	Carbon Reduction, Volatilisation and Reoxidation	—	Calcination (ZnO)	
	Zinciferous Lead Slags	Carbon Monoxide Reduction, Volatilisation and Reoxidation	—		

Roasting and other Chemical Processes preceding Reduction to Metal

Roasting is defined as heating a material without fusion for the purpose of adding to it some desired element, or elements, usually oxygen. It thus differs from calcination which is heating a material in order to effect a decomposition Roasting is usually undertaken in order to effect the complete, or partial, removal of sulphur or some similar element, such as arsenic or tellurium, as a volatile oxide.

Rapid and complete oxidation would require fine particle size, constant stirring of the bed to expose the lower layers of ore and a rapid flow of air for the removal of the gaseous products of combustion. Practical considerations, however, limit these conditions, for fine grinding is expensive, and all three would promote heavy dusting loss and so add to the cost of the operation. It follows that complete elimination of the undesired element is not practicable. If sufficient sulphur is present, the heat generated by combustion, once this has started, may be sufficient to carry oxidation through, nearly to completion. This " autogenous " roasting is economical but needs control, for overheating and fusion would diminish the surface area exposed and would " blanket," or protect, unoxidised particles. The admission of excess cold air, or the circulation of waste furnace gas that is deficient in oxygen, may rectify matters. Alternatively, the addition of incombustible material or of material that will decompose with the absorption of heat will lower the temperature attained. Conversely, the introduction of some carbonaceous fuel may diminish sulphur elimination by impoverishing the atmosphere in oxygen. The importance of a knowledge of equilibrium conditions and of reaction kinetics in such operations is evident and attention must also be paid to the many possible subsidiary reactions that will result from the presence of impurities. A new method for studying the mechanism of roasting reactions, involving a direct examination of changes in the composition of cylindrical briquettes after various periods of roasting, has been put forward by Peretti.[15]

Sulphating roasting usually precedes hydro-metallurgical treatment. It presents the usual roasting problems but conditions must be so adjusted that sulphate formation is encouraged. Chloridising roasting requires analogous conditions and, in both cases, the addition of catalytic agents may be advisable or necessary, thus introducing a new series of problems.

Flash roasting and sintering are roasting treatments effected under rather different operating conditions. In the former, finely divided mineral is injected into an oxidising atmosphere that is at such a temperature that combustion is immediate and almost complete. In the latter, one surface of a bed of charge is heated to the ignition temperature and air is forced through so that the zone of combustion progresses to the further surface of the bed. In this operation the primary, or only, purpose may be to cause agglomeration of the charge.

Volatilising roasting is a controlled roast used for the production and removal of a volatile oxide, such as arsenious oxide. In addition to the usual roasting problems, this operation raises further questions in the field of condensation, dust and fume recovery and the like. Excessive oxidation may form a non-volatile, higher oxide, and careful control is, therefore, needed to avoid the necessity for retreatment under reducing conditions.

Reduction Processes

The most familiar procedure under this heading is smelting : heating a material under such conditions that, in addition to chemical change, there is complete fusion so that separation of the metal can be effected by gravitational flow. It is usually necessary to add fluxes for the formation of a slag that is suitably fluid at the working temperature, and a reducing agent may be needed to bring the metal to the elemental state. As a means for the production of metal, smelting is generally applied to oxidised ores or to material that has been roasted to convert the metal to oxide, and carbon in the form of coke is normally the reducing agent as well as the source of heat.

Where a metal has a strong affinity for sulphur or for arsenic or antimony, it may be separated as a sulphide by "matte smelting," or as an arsenide or antimonide by "speise smelting." In "pyritic" matte smelting, the sulphur of the ore is both the reducing agent and the fuel, only a minimum of carbon being needed. The particular advantage of such procedures lies in the ready, and almost complete, collection of the sulphides of metals whose oxides would be dissolved by, and retained in, the slag.

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[15] This Discussion.

It is usual in smelting operations to separate the maximum of unwanted matter as a waste slag, but it is sometimes advantageous, as in the case of tin, to work under only mildly reducing conditions, whereby a cleaner metal is obtained. The "foul" slag, containing a high proportion of metal oxide, is retreated for the recovery of a lower grade, but still saleable, metal The control of the grade of pig-iron by adjustment of the proportion of carbonaceous fuel and fluxes is familiar, but there are few analogous cases in non-ferrous smelting. The principal problems in these operations are concerned with the composition and resulting physical properties of the slag, and the effect of these on the slag-metal equilibrium which governs the magnitude of the slag loss.

The Waelz process is one in which reduction is not accompanied by fusion, although there is usually agglomeration, and it can be used for a variety of purposes. Carbon is mixed with the ore which is passed through a cylindrical furnace. Iron is reduced to metallic powder form, as in the Krupp and other processes for the reduction of iron ores with natural or artificial gas, and is recoverable by magnetic concentration. Zinc is reduced, volatilised, re-oxidised in the furnace atmosphere and collected as fume, and other metals can be recovered by suitable adjustment of the operating conditions.

The use of selective flotation for the treatment of complex lead ores has, by the removal of copper, made possible the smelting of zincy lead concentrates. The zinc content of the resulting lead blast-furnace slag commonly runs as high as 20 %. This zinc is recovered by "fuming," air and powdered coal in the proportions necessary to form carbon monoxide being blown into the molten slag. Zinc is reduced, volatilised, re-oxidised above the bath and recovered as fume. As in the Waelz process, the recovery of zinc is effected by much the same method as that adopted for its collection from scrap brass, and it presents similar problems in dust and fume recovery.

Reference to Fig. 1 shows the exceptional position of carbon as a general reducing agent for metallic oxides. The composite curve for the oxidation of carbon to the equilibrium $CO-CO_2$ mixture runs down across the diagram owing to the increase in the standard free energy of formation of CO with rise in temperature and thus comes, at sufficiently high temperatures, below the lines for the oxidation of even the most reactive metals. Thus, the C–CO line intersects the Mg–MgO line below 2000° c., and above this temperature magnesium oxide can be reduced by carbon giving magnesium vapour and CO. This process presents special difficulties owing to the tendency for the reverse reaction, $Mg + CO = MgO + C$, to occur during the cooling of the gases, unless the temperature is brought down very rapidly below the boiling point of magnesium by "shock" cooling with cold hydrogen.

It is noteworthy that although zinc has not a very great affinity for oxygen, its high volatility results in the intersection of the C–CO and the Zn–ZnO lines being slightly above the boiling point of the metal. It is for this reason that, unless conducted under pressure, the reduction of zinc oxide with carbon necessarily yields the metal in the form of vapour and the operation becomes a distillation process. In many respects volatilisation of the metal is an advantage in that it provides an effective means of separation, but the vapour pressures (at the working temperature) of other metals present are important, for these govern the purity of the product. Also the re-oxidation of zinc, especially by carbon dioxide which is commonly present above the equilibrium concentration owing to incomplete establishment of equilibrium with carbon, occurs readily on cooling the mixed gases, and gives rise to contamination with "blue powder."

Comparison of Fig. 1 and 2 affords an explanation of the relative inadequacy of carbon as a reducing agent for sulphides; the free energy of formation of carbon bisulphide is very small and there is no monosulphide to correspond with CO. Moreover, as the lines for the metallic sulphides are more closely bunched together than are those for oxides, the possibilities of separation by preferential reduction are much less. It is for these reasons that sulphide ores and mattes are commonly converted to oxides by a roasting operation before being reduced to metal. Similar arguments apply—probably more strongly—to arsenides and antimonides. An example of the direct reduction of a sulphide is afforded, however, by the reducing fusion of antimony sulphide with metallic iron.

For the nobler metals, reduction of oxides or sulphides may be effected merely by the application of heat. Thus from the lines in Fig. 1 and 2 representing compounds of those metals, it is seen that the free energies of formation fall to zero at moderate temperatures, and it should, therefore, be possible to dispense with any reducing agent. Mercury sulphide decomposes at a moderate temperature, the metal being volatilised and recovered by condensation. The distillation of metallic arsenic from mispickel is similar but this metal is so readily oxidised that reducing conditions must be ensured by the addition of some carbonaceous fuel.

In the Bessemerisation of copper matte, the initial stage is the oxidation of impurities which are removed in the slag and fume, and this is followed by partial conversion of Cu_2S (white metal) to Cu_2O; these two substances then interact to form metal ($Cu_2S + 2Cu_2O = 6Cu + SO_2$). An analysis of the reactions in the converting of copper matte has been made by Peretti.[16] From a combination of data from Fig. 1 and 2 it can be shown that the mutual oxide-sulphide reduction is possible for lead and nobler metals but not for more reactive metals such as nickel.

Although carbon is able to reduce the oxides of even the most reactive metals if a sufficiently high temperature is employed, the disadvantages of operation at very high temperatures may lead to alternative reducing agents being preferred. Even for metals that are not highly reactive, other reducing agents may commend themselves for special reasons; thus, where hydro-metallurgical methods are used, the metal may be recovered from aqueous solutions by cementation (precipitation by a baser metal, e.g., copper by iron) or by electrolysis (e.g., zinc). It is for metals notably more reactive than zinc, however, that alternatives to carbon begin to be generally attractive. Thus Table II indicates the use of hydrogen in a few instances, as in the production of tungsten; of aluminium in the Thermit process for production of metals such as molybdenum and titanium; and of ferro-silicon for making such ferro-alloys as ferro-chromium and ferro-vanadium. In the Thermit process the heat of reaction is often so great that no additional flux is necessary to ensure separation but, as in ordinary smelting, metals of lower oxygen-affinity will also be reduced. It is usual, therefore, to precede such treatments by a chemical operation for the removal of those undesirable impurities that would pass into the metal. Hydrogen is less favoured as a general reducing agent as it is liable to be retained in solution in some metals and this often has deleterious effects.

From Fig. 1 the reduction of magnesium oxide by silicon to yield magnesium vapour would seem to require a fairly high temperature even under a pressure as low as 0·001 atm. In the Pidgeon process, however, using ferro-silicon, the process is successfully operated on calcined dolomite at much lower temperatures. This is presumably due not only to the rapid removal of magnesium from the sphere of action but also to the activity of the other product, silica, being kept extremely low by reaction with lime to form a stable calcium silicate. Condensation in a closed system is less troublesome than in the open condensers of the zinc reduction process and there is a great advantage over reduction of magnesia with carbon in that, as there is only one gaseous product, no question arises of interactions in the gas phase on cooling. The vapour pressure of magnesium in the thermal reduction of dolomite by ferro-silicon is the subject of a paper by Pidgeon and King.[17]

Finally, for the extraction of the most highly reactive metals, electrolysis of a molten salt system continues to be the most common practice. In many cases the bath consists of a molten chloride or a low-melting mixture of molten halides, but the molten hydroxide is still largely employed for sodium and a

[16] This Discussion.

[17] This Discussion.

saturated solution of the oxide in a halide melt for aluminium. For reductions of the last type, the minimum voltage required for decomposition can be read directly from the voltage scale on Fig. 1 but this would refer to breaking down into the metal and oxygen at 1 atm. pressure. For the overall reaction $Al_2O_3 + 3C = 2Al + 3CO$ which results from the use of carbon anodes, the decomposition voltage at a specified temperature is given by the vertical distance between the $Al-Al_2O_3$ and the C–CO curves. In practice, much larger voltages are required for electrolysis at a reasonable current density, due to resistance of the melt and to the polarisations involved.

Diagrams such as Fig. 1 and 2 can clearly be used as guides in making improvements in existing processes and in exploring the possibilities of new developments. Thus, Fig. 2 indicates the minimum voltages required at various temperatures to decompose sulphides into the metal and gaseous sulphur, and the paper by Davis, Rose and Ellingham[11] shows that results of measurements of the decomposition voltage of sulphides dissolved in chloride melts accord reasonably well with values calculated from standard free-energy data. The possibilities of the electrolytic decomposition of lead sulphide (dissolved in lead chloride) into lead and sulphur (the Halkyn process) have received some attention.

In assessing the merits of new extraction schemes, however, the thermodynamic data provide only an initial guide, particularly by excluding the impossible. Such information needs to be supplemented by measurements or calculations of reaction rates, and in any event the determining factor will normally be the extent to which separation from undesired elements can be readily effected. The importance of this factor cannot be over-emphasised for the cleaner ore-deposits are mostly exhausted. Mineral dressing operations, even if they were completely efficient, could give no more than a clean mineral, and if this mineral is complex, the physico-chemical considerations are consequently less simple. Further, the development of new processes is calling for ever closer collaboration among a wide range of scientists and technologists, and it is on this collaboration that the future of extraction metallurgy will depend.

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GRAPHICAL STUDY OF METALLURGICAL EQUILIBRIA

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In 1912 Le Chatelier[1] showed the value of the concept of " equilibrium oxygen pressure " in the study of oxidation equilibria in the presence of a gaseous phase. The conditions of stability of metallic oxides are usually expressed graphically by plotting the logarithm of the oxygen pressure as ordinate and the temperature as abscissa ; thus the conditions of stability of FeO, first elucidated by Chaudron[2] [3] have been expressed in this way by different authors.[4] [5] [6] These diagrams are particularly easy to interpret if, as was already done 35 years ago by the schools of Le Chatelier in France and Scheffer in Holland, the abscissa is plotted, not as the temperature, but as $1/T$, the inverse of the absolute temperature: diagrams are thus obtained which consist of nearly straight lines, the slopes of which represent heat content changes and the intercepts on the y-axis entropies changes of the reactions.

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[1] Le Chatelier, *Rev. Métall.*, 1912, **9**, 509.
[2] Chaudron, *Compt. rend.*, 1921, **1**, 152.
[3] Chaudron, *Ann. Chim.*, 1921, **16**, 221.
[4] Van Gronigen, *Thesis* (Delft, 1921).
[5] Schenck, *The Physical Chemistry of Steelmaking* (J. Springer, Berlin, 1932), vol. 1.
[6] Chaudron, in Pascal's *Treatise of Mineral Chemistry* (Massau, Paris, 1934), **12**, p. 184.

In previous publications, one of the authors has described a method for the study of "complex equilibria" based on this method and dealing with 1-, 2- or 3-component systems.[7] [8] [9] [*] This method depends on the fact that the equilibrium characteristics of each transformation that can occur in the system are expressed in terms of these two functions (the logarithm of the equilibrium oxygen pressure and $1/T$); these two factors are considered as independent variables and other relevant factors as parameters. By plotting the values of these two variables, curves are obtained which yield an overall picture of the conditions of thermodynamical stability of all the substances taking part.

The method of setting-up such diagrams has been described previously,[9] and Fig. 1 and 2 are examples of the binary systems, zinc-oxygen and carbon-oxygen; Fig. 3 relating to the ternary system zinc-carbon-oxygen was obtained by a superimposition of Fig. 1 and 2, and by the simultaneous introduction of the conditions under which the ternary compound $ZnCO_3$ is stable.

These diagrams are based on the equilibrium equations given below, in which p represents the partial pressure (or, more precisely, the fugacity) of the different gases. These equations are valid only in the temperature ranges described elsewhere;[9] where great precision is required it is necessary to construct large-scale diagrams based on the more complicated equations which would produce slightly curved instead of straight lines; at present, where the principle of this method is the main consideration, the simplified equations below are assumed to be sufficiently exact.

[†] **Zinc-Oxygen System** (Fig. 1)

EQUILIBRIA BETWEEN TWO CONDENSED SUBSTANCES

$Zn(s) \rightarrow Zn(l)$ $\quad 0 = -\frac{1000}{T} + 1{\cdot}445$ . . . (a)

$2Zn(s) + O_2 \rightarrow 2ZnO(s)$ $\quad \log p_{O_2} = -\frac{34{,}900}{T} + 8{\cdot}70$ . . (b)

$2Zn(l) + O_2 \rightarrow 2ZnO(s)$ $\quad \log p_{O_2} = -\frac{35{,}970}{T} + 10{\cdot}24$ . . (c)

EQUILIBRIA BETWEEN ONE CONDENSED AND ONE GASEOUS SUBSTANCE (OTHER THAN O_2)

$Zn(s) \rightarrow Zn(g)$ $\quad 0 = -\frac{6810}{T} + 6{\cdot}10 - \log p_{Zn}$. (a)

$Zn(l) \rightarrow Zn(g)$ $\quad 0 = -\frac{6275}{T} + 5{\cdot}33 - \log p_{Zn}$. (b)

$2Zn(g) + O_2 \rightarrow 2ZnO(s)$ $\quad \log p_{O_2} = -\frac{48{,}520}{T} + 20{\cdot}90 - 2\log p_{Zn}$ (e)

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[7] Pourbaix, *Bull. Soc. chim. Belg.*, 1944, **53**, 145.

[8] Pourbaix, *Rev. Métall.*, 1947, 292.

[9] Pourbaix, *Complex Chemical Equilibria. Method of Calculation and Graphical Representation* (Ed. Science et Technique, Brussels, 1948).

[10] Montagne, *Numerical Calculations of Homogeneous Chemical Equilibria; Application to the Theoretical Study of Combustion.* (Ed. Gauthier-Villars, Paris, 1934.)

[11] Ellingham, *Trans. Soc. Chem. Ind.*, 1944, **63**, 125.

[*] It should be noted that Montagne[10] published in 1934 another graphical method of calculating complex equilibria in a homogeneous gas phase. In 1944 Ellingham[11] published diagrams showing the influence of temperature on the free energies of formation of different oxides and sulphides; this paper makes an important contribution to the study of the complex equilibria prevailing in thermal metallurgy.

[†] Log denotes $\log_{10}$ throughout.

Carbon-Oxygen System (Fig. 2)

EQUILIBRIA BETWEEN SOLID CARBON AND ONE GAS (OTHER THAN O_2)

$$C(s) = C(g) \qquad 0 = \frac{42{,}960}{T} - 8{\cdot}02 + \log p_{C} \qquad (a)$$

$$2C(s) = C_2(g) \qquad 0 = \frac{49{,}350}{T} - 8{\cdot}98 + \log p_{C_2} \qquad (b)$$

$$2C(s) + O_2 = 2CO \qquad \log p_{O_2} = -\frac{11{,}200}{T} - 9{\cdot}64 + 2\log p_{CO} \qquad (c)$$

$$C(s) + O_2 = CO_2 \qquad \log p_{O_2} = -\frac{20{,}280}{T} - 0{\cdot}34 - \log p_{CO_2} \qquad (d)$$

EQUILIBRIA BETWEEN TWO GASES (OTHER THAN O_2)

$$2CO + O_2 = 2CO_2 \qquad \log p_{O_2} = -\frac{29{,}360}{T} + 8{\cdot}96 - 2\log\frac{p_{CO_2}}{p_{CO}} \qquad (e)$$

$$2C(g) + O_2 = 2CO \qquad \log p_{O_2} = -\frac{97{,}120}{T} + 6{\cdot}40 + 2\log\frac{p_{CO}}{p_{C(g)}} \qquad (f)$$

$$C_2(g) + O_2 = 2CO \qquad \log p_{O_2} = -\frac{60{,}550}{T} - 0{\cdot}66 + \log\frac{p^2_{CO}}{p_{C_2(g)}} \qquad (g)$$

$$2C(g) = C_2(g) \qquad 0 = -\frac{36{,}570}{T} + 7{\cdot}06 - \log\frac{p^2_{C(g)}}{p_{C_2(g)}} \qquad (h)$$

Eqn. (*a*) and (*b*) relating to the vapour pressure of zinc are only approximate Where greater precision is necessary it would be better to use more complex equations such as those of Maier (ref. 9, p. 28).

Zinc-Carbon-Oxygen System (Fig. 3)

EQUILIBRIA BETWEEN TWO CONDENSED SUBSTANCES

$$Zn(s) = Zn(l) \qquad 0 = -\frac{1000}{T} + 1{\cdot}445 \qquad (a)$$

$$2Zn(s) + O_2 = 2ZnO(s) \qquad \log p_{O_2} = -\frac{34{,}900}{T} + 8{\cdot}70 \qquad (b)$$

$$2Zn(l) + O_2 = 2ZnO(s) \qquad \log p_{O_2} = -\frac{35{,}970}{T} + 10{\cdot}24 \qquad (c)$$

$$ZnCO_3(s) = ZnO(s) + C(s) + O_2 \qquad \log p_{O_2} = -\frac{28{,}360}{T} + 13{\cdot}84 \qquad (d)$$

EQUILIBRIA BETWEEN ONE CONDENSED AND ONE GASEOUS SUBSTANCE (OTHER THAN O_2)

$$2C(s) + O_2 = 2CO \qquad \log p_{O_2} = -\frac{11{,}200}{T} - 9{\cdot}64 + 2\log p_{CO} \qquad (e)$$

$$C(s) + O_2 = CO_2 \qquad \log p_{O_2} = -\frac{20{,}280}{T} - 0{\cdot}34 + \log p_{CO_2} \qquad (f)$$

$$Zn(s) = Zn(g) \qquad 0 = -\frac{6810}{T} + 6{\cdot}10 - \log p_{Zn} \qquad (g)$$

$$Zn(l) = Zn(g) \qquad 0 = -\frac{6275}{T} + 5{\cdot}33 - \log p_{Zn} \qquad (h)$$

$$2Zn(g) + O_2 = 2ZnO(s) \qquad \log p_{O_2} = -\frac{48{,}520}{T} + 20{\cdot}90 - 2\log p_{Zn} \qquad (k)$$

$$ZnCO_3(s) = ZnO(s) + CO_2 \qquad 0 = -\frac{8080}{T} + 14{\cdot}18 - \log p_{CO_2} \qquad (l)$$

EQUILIBRIA BETWEEN CONDENSED AND TWO GASEOUS SUBSTANCES (OTHER THAN O_2)

$$Zn(g) + C(s) + O_2 = ZnO(s) + CO \qquad \log p_{O_2} = -\frac{29{,}860}{T} - 5{\cdot}63 + \log\frac{p_{CO}}{p_{Zn}} \qquad (m)$$

$$2Zn(g) + 2C(s) + O_2 = 2Zn(l) + 2CO \; \log p_{O_2} = -\frac{23{,}750}{T} + 1{\cdot}02 + 2\log\frac{p_{CO}}{p_{Zn}} \qquad (n)$$

EQUILIBRIUM BETWEEN TWO GASES (OTHER THAN O_2)

$$2CO + O_2 = 2CO_2 \qquad \log p_{O_2} = -\frac{29{,}360}{T} + 8{\cdot}96 + 2\log\frac{p_{CO_2}}{p_{CO}} \quad . \quad (p)$$

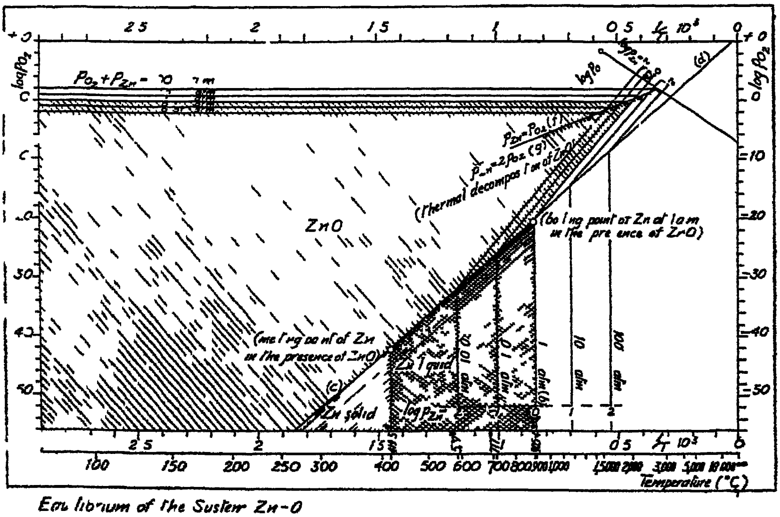
In the Figures the following curves are shown

1. *Heavily drawn* are straight lines which separate the regions of stability of the different condensed substances of which the system consists
2. *Less heavily drawn* are groups of straight lines which represent the composition of the various gases, some of those lines along which the partial pressures of the two gases are equal, separate the 'regions of predominance'
3. *Lightly drawn* are groups of straight lines which show the conditions under which, in the presence of the different condensed substances, the partial pressures of the different gases have fixed values
4. *Very heavily drawn* are isobars for which, in the presence of different condensed substances, the total pressure of the gases considered has a determined value

   These isobars consist of fragments of virtually straight lines with different slopes, these fragments meeting in a sharp angle or joined to each other by curves
5. *In dotted lines*, the lines which express the conditions under which a condensed substance or a gas decomposes or dissociates into gaseous constituents

Some facts emerging from these diagrams are briefly summarised

Zinc-Oxygen System (Fig 1) On heating ZnO to a high temperature in surroundings initially free of zinc, oxygen or any of their derivatives apart from ZnO, it decomposes with the formation of zinc vapour and oxygen according to the reaction, $2ZnO(s) = 2Zn(g) + O_2$ as shown by curve (g), the decomposition pressure varies as a function of the temperature according to the equation:



Equilibrium of the System Zn-O

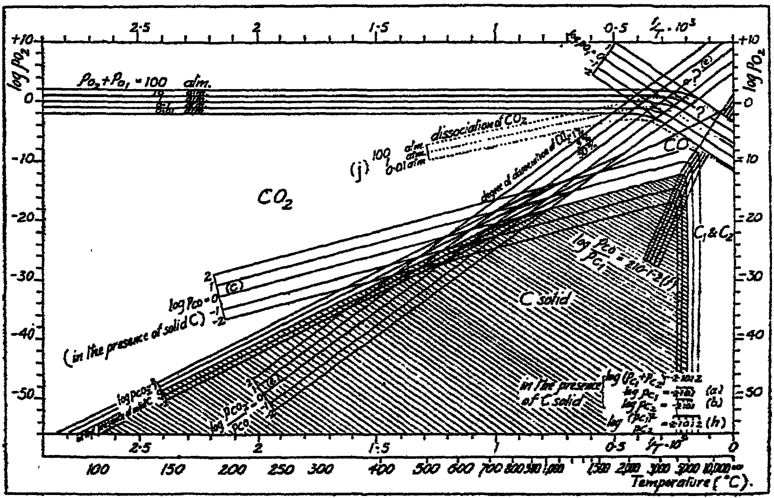
FIG. 1

$$\log P = -\frac{16{,}173}{T} + 7{\cdot}24.$$

This pressure reaches 0·01 atm at about 1477° C. and 1 atm at about 1962° C.

If the ZnO is heated in the presence of 1 atm. oxygen, the system no longer follows curve (*g*) but the upper branch of the isobar relating to 1 atm.; the ZnO remains stable up to the temperature at which this isobar ceases to be a straight line, then it becomes curved, denoting that a perceptible quantity of zinc vapour has been formed; at all points on the diagram the partial pressure of zinc vapour in the presence of ZnO is given by the index of the particular member of the group of curves (*e*) which passes through this point; at 1477° c., the zinc vapour pressure, which is equal to $10^{-2.18}$ atm. (0·0066 atm.) when the heating is performed in an inert atmosphere, becomes $10^{-3.42}$ atm. (0·00038 atm.) when the heating is performed in 1 atm. oxygen pressure.

Carbon-Oxygen System (Fig. 2). The oxidation of solid carbon yields CO_2 at low temperatures, and CO at high temperatures; above 5000–10,000° c., carbon vaporises forming mono- and di-atomic molecules which are probably stable, even in the presence of free oxygen; CO and O_2 are then partially or totally dissociated into O(*g*), C(*g*) and C_2(*g*).



Equilibrium of the System C-O.

FIG. 2.

In the presence of an excess of solid carbon, free oxygen is not stable, except probably in low concentrations of the atomic form O(*g*), at temperatures between 3000–4000° c. The effect of temperature on the relative proportions of CO and CO_2 in equilibrium with solid carbon at a fixed pressure (the Boudouard equilibrium) can be determined by reading on the diagrams, along the isobar relating this pressure, the value of the indices of the lines of the group (*e*).

If pure CO_2 at a fixed pressure is heated, reaction proceeds in a manner denoted by the curve of the group (*j*) corresponding to this pressure. The CO_2 remains stable up to the temperature at which this curve begins to show a perceptible curvature. This curvature denotes the production of an appreciable quantity of CO, resulting from the dissociation of CO_2, according to the reaction:

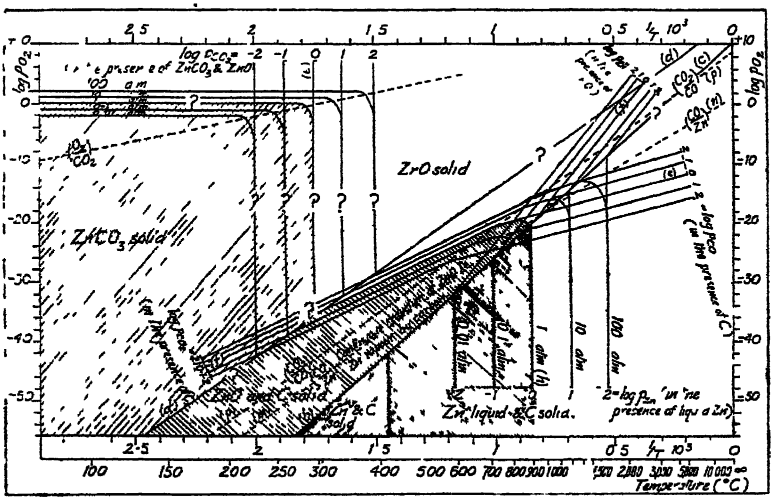
$$2CO_2 = 2CO + O_2.$$

At all points on this line, the degree of dissociation of CO_2 is given by the index of the line of the group *e* which passes through this point. Near 2000° c. (under 1 atm. pressure) there appears an appreciable proportion of monatomic oxygen, and between about 4000–6000° c. it is probable that the dissociation of CO_2 viz., CO_2 = CO + O(*g*), is appreciable. It is probable that at about 8000° c., dissociation of CO takes place with the formation of carbon vapour.

Zinc-Carbon-Oxygen System (Fig. 3). Zinc carbonate, $ZnCO_3$, is the thermodynamically stable solid at room temperature in presence of 1 atm. O_2, on heating, it decomposes according to

$$ZnCO_3(s) = ZnO(s) + CO_2$$

probably with formation of solid solutions. ZnO is stable in the presence of solid carbon and under a pressure of (CO_2 + CO + Zn(g)) equal to 1 atm. in that region of the diagram bounded by curves d, b and c and by the isobar for 1 atm. On heating, ZnO is reduced by the carbon with simultaneous formation of CO, CO_2 and zinc vapour according to the conditions which are approximately shown by curve m; at each temperature the pressures of CO, CO_2 and Zn vapour and the total pressure of (CO + CO_2 + Zn(g)) are shown by the four members of the groups of curves which pass through the points of the curve m corresponding



Equilibrium of the System Zn-O-C

FIG. 3.

to this temperature; the influence of the temperature on the pressure due to the reduction of ZnO to Zn vapour can be expressed reasonably well by the equation:

$$\log P = \frac{9330}{T} - 7{\cdot}935,$$

which gives values similar to those obtained in 1938 by Decroly and by Meunier.

At the point where curve m meets curve c, liquid Zn appears (t = 1049° c., P = 7·5 atm.). As was found by Decroly and Meunier, the reduction of ZnO by carbon then proceeds with the simultaneous formation of zinc vapour and liquid zinc, as shown by curve c; from these lines, one can determine at each temperature the pressures of CO, CO_2 and zinc vapour, and, consequently, the total pressure and the yield of liquid zinc.

Curves b and c show the conditions governing the equilibrium between zinc oxide and solid, or liquid, zinc; the pressures of CO_2 and CO at various points on this curve are thus those above which CO_2 and CO will oxidise metallic Zn; for example, a gas containing 99 % nitrogen and 1 % CO under atmospheric pressure (when $\log p_{CO} = -2$) will or will not oxidise zinc according to whether the temperature is greater or less than 764° c.

Isobars

(1) General Trends of the Isobars. The isobars denote the oxygen pressure and temperature at which the various condensed substances (solids and liquids) are in equilibrium with an atmosphere in which the sum of the partial pressures of the various gases is fixed.

These curves are inscribed in a polygon consisting of straight-sided * segments each of which corresponds to the equilibrium of a condensed phase with a gas at a constant partial pressure. In those regions of the diagrams in which the composition of the system does not vary appreciably, the isobars are virtually identical with these segments; they are then therefore virtually straight lines along which the composition of the system hardly changes. Any perceptible variation in the reacting system produces an appreciable change in the slope of the isobars. This change is sharp when the composition of the system alters sharply, i.e., when a condensed phase appears or disappears; the isobars thus have points of discontinuity where they cross the limits of stability of the condensed phases. This change of slope is gradual when the composition of the system alters gradually, i.e., when there is a change in the composition in the gas phase, in a solid solution or in a liquid solution. The isobars then display a curvature in the neighbourhood of their crossing of the limits separating the regions in which different gases predominate.

EXAMPLES.—(1) In Fig. 1, relating to the zinc-oxygen system, curve *d* separates the regions in which liquid zinc and solid zinc oxide are stable, and curve *f* separates the regions in which gaseous zinc or oxygen gas predominate in the presence of solid zinc oxide; the isobars thus cross curve *d* at a point of discontinuity and are curved in the vicinity of their intersection with curve *f*.

(2) In Fig. 2, relating to the carbon-oxygen system, the curve *e*, with the index zero, separates the regions in which CO_2 and CO predominate, and the curve *f*, with the index zero, separates the regions in which CO and C(*g*) predominate. The isobars therefore display a curvature in the vicinity of their intersections with the curves *e* and *f* with the index zero.

(ii) Inclined, Vertical and Horizontal Branches. All curves drawn represent the equilibrium conditions of a transformation or group of transformations of which the heat content (or heat of transformation at constant pressure) expressed in terms of 1 g. mol. O_2 liberated, is given in sign and magnitude by the slope of this curve. A slope of unity corresponds to a quantity of heat absorbed equal to 4575 cal./g. mol. O_2 combining in the reaction.

A curve rising from left to right corresponds to the equilibrium of an exothermic oxidation reaction; and one falling from left to right to that of an endothermic oxidation reaction. A vertical curve corresponds to an equilibrium in which free O_2 does not take part (and for which Q/n, where Q is the heat of transformation per n g mol. O_2, is thus infinite). A horizontal curve corresponds to an equilibrium occurring without liberation or absorption of heat (and for which Q/n is thus zero).

It is thus evident that the inclined curves represent oxidation equilibria, the vertical curves represent equilibria of vaporisation or dissociation not involving free O_2, and the horizontal curves represent transformation taking place without the absorption or evolution of heat.

EXAMPLES.—(1) In Fig. 1, relating to the zinc-oxygen system, the vertical branches *b* correspond to the vaporisation of metallic zinc; the inclined curves *c* correspond to the exothermic oxidation of zinc vapour to solid ZnO; the horizontal branches which are the upper portions of the isobars correspond to an increase or decrease of the partial pressure of oxygen by non-chemical causes, without evolution or absorption of heat.

(2) In Fig. 2, relating to the carbon-oxygen system, the branches *d* of the isobars which rise steeply correspond to the strongly exothermic reaction, $C + O_2 = CO_2$, the less steep branches *c* correspond to the less exothermic reaction, $2C + O_2 = 2CO$, and the vertical branches to the vaporisation of solid carbon to C(*g*) or C_2(*g*).

Hence by inspection of a diagram it is possible to tell whether, for instance, an oxide will or will not decompose on heating; e.g., when the region of stability of an oxide is bounded on the right by sloping isobars, this oxide is decomposed by heat with gaseous components (as, for example, with CdO, HgO, ZnO and CaO which decompose on heating to give the metallic vapour and oxygen). On the other hand, when the region of stability of an oxide is bounded on the right by vertical isobars, the oxide is vaporised by heat without decomposition (as for PbO and MoO_3, and, except under very strongly reducing conditions, for H_2O).

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* In the cases where Scheffer's rule does not apply these segments are not straight, but are more or less curved.

(iii) **Points Having Horizontal or Vertical Tangents.** Certain of the isobars have horizontal or vertical tangents.

(*a*) HORIZONTAL TANGENTS. It may be shown that a point on a curve having a horizontal tangent corresponds to the attainment of an equilibrium by a group of endothermic and exothermic reactions in such a way that the sum of the heat changes of these reactions is zero; thus the relative quantities of substances taking part in the various reactions is such that the heat liberated by the exothermic reactions is equal to the heat absorbed by the endothermic reactions.

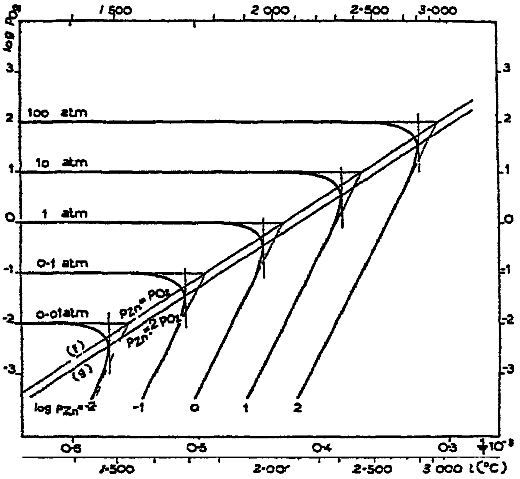

FIG. 4.—Zinc-oxygen equilibrium (detail).

In the case of a number of reactions written in the form:

$$O_2 + n_1 B_1 + \Sigma \nu_1 M_1 = 0$$

$$O_2 + n_2 B_2 + \Sigma \nu_2 M_2 = 0$$

in which there take part *n* molecules of a gaseous substance B and ν of the condensed substances M, per molecule of diatomic oxygen O_2 involved, and of which the heat contents are respectively ΔH_1, ΔH_2, etc., this condition can be expressed analytically as will be shown below, as

$$\Sigma \frac{\Delta H \cdot p_B}{n} = 0$$

EXAMPLES.—(1) In Fig. 2 and 5 relating to the *carbon-oxygen* system, each isobar has a point at which the tangent is horizontal and at which the sum of the three reactions:

$$2C(s) + O_2 = 2CO \quad (\Delta H = 11{,}200 \times 4{\cdot}575)$$

$$C(s) = C(g) \quad (\Delta H = -42{,}960 \times 4{\cdot}575)$$

$$2C(s) = C_2(g) \quad (\Delta H = -49{,}350 \times 4{\cdot}575)$$

takes place without the evolution or absorption of heat. This condition is fulfilled when

$$\frac{11{,}200}{-2} \times p_{CO} + \frac{-42{,}960}{-1} \times p_{C(g)} + \frac{-49{,}350}{-1} \times p_{C_2(g)} = 0$$

(2) In Fig. 3 and 6, relating to the *zinc-carbon-oxygen* system each isobar has a point whose tangent is horizontal at which the three reactions:

$$C(s) + O_2 = CO_2 \quad (\Delta H = 20{,}280 \times 4{\cdot}575)$$

$$2C(s) + O_2 = 2CO \quad (\Delta H = 11{,}200 \times 4{\cdot}575)$$

$$2ZnO(s) = 2Zn(g) + O_2 \quad (\Delta H = -48{,}520 \times 4{\cdot}575)$$

takes place without the evolution or absorption of heat. This condition is fulfilled when

$$\frac{20{,}280}{-1} \times p_{CO_2} + \frac{11{,}200}{-2} \times p_{CO} + \frac{48{,}520}{2} \times p_{Zn} = 0$$

(*b*) VERTICAL TANGENTS. A point on a curve at which the tangent is vertical corresponds to the case where the sum of the transformations in the system takes place *without exchange of oxygen* (or other substances) with its surroundings. The partial pressures of each of the reacting substances then have values corresponding stoichiometrically to the quantities required by the possible reactions. As will be shown below this condition can be expressed analytically as

$$\sum \frac{p_B}{n} = 0$$

EXAMPLES.—(1) In Fig. 1 and 4 relating to the *zinc-oxygen* system, each isobar displays at the top right-hand portion a point at which the tangent is vertical; here solid ZnO is in equilibrium with an atmosphere of zinc vapour and oxygen, at partial pressures such that

$$\frac{p_{O_2}}{-1} + \frac{p_{Zn}}{2} = 0$$

$$\text{i.e., } p_{Zn} = 2p_{O_2}$$

The locus of points in Fig. 1 and 4 at which the isobars have vertical tangents thus represents the conditions under which the thermal decomposition of ZnO can occur according to $2ZnO \rightarrow 2Zn(g) + O_2$ in surroundings initially free of zinc and/or oxygen compounds other than ZnO. It may be shown on the basis of the equations from which this diagram was constructed that this locus is a straight line:

$$\log p_{O_2} = -\frac{16{,}173}{T} + 6{\cdot}77,$$

from which it may be shown that

$$\log (p_{O_2} + p_{Zn}) = -\frac{16{,}173}{T} + 7{\cdot}24;$$

this equation expresses the effect of temperature on the decomposition pressure of ZnO.*

(2) In Fig. 3 and 6 relating to the *zinc-carbon-oxygen* system, the isobars representing pressures not greater than 7·5 atm. have in the centre of the diagram points at which their tangents are vertical, and carbon and ZnO are in equilibrium with an atmosphere in which carbon dioxide, carbon monoxide and zinc vapour occur with partial pressures given by

$$\frac{p_{CO_2}}{-1} + \frac{p_{CO}}{-2} + \frac{p_{Zn}}{2} = 0$$

$$\text{i.e., } p_{Zn} = p_{CO} + 2p_{CO_2}.$$

The locus of points in Fig. 3 and 6 at which the isobars have vertical tangents represents the conditions under which zinc oxide can be reduced by carbon through the reactions,

$$2ZnO + 2C = 2Zn(g) + 2CO$$

$$\text{and } 2ZnO + C = 2Zn(g) + CO_2,\dagger$$

in surroundings initially free from compounds of zinc, carbon and/or oxygen other than ZnO and C. By measurements along curve *m*, which is the locus of these points, it is thus possible to determine the influence of temperature on the composition of the gas-phase (i.e., on the partial pressures of CO_2, CO and Zn(*g*) and the total pressure). It must be remembered, however, that curve *m* expresses the conditions of reduction of ZnO only in those parts of the diagram where ZnO is a stable condensed phase, i.e., to the left of the point of intersection of this curve *m* and curve *c* ($T = 1049°$ c., $P = 7{\cdot}5$ atm.). Above this point the reduction results in the formation of liquid zinc, as has been established by Decroly [12] and Meunier,[13] and the conditions of equilibrium for this reaction are represented by curve *c*.

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[12] Dony Hénault and Decroly, *Experimental Researches on the Metallurgy of Zinc* (Liège, 1938).

[13] Meunier, *Bull. Soc. chim. Belg.*, 1938, **47**, 99.

* Ref. [9].

† It is well known that this reaction consists of the two consecutive reactions $ZnO + C = Zn(g) + CO$ and $ZnO + CO = Zn(g) + CO_2$; this does not affect in any way the validity of thermodynamical study of the overall reaction, $2ZnO + C = 2Zn(g) + CO_2$.

As is shown by the two preceding examples, those points on the diagram at which the isobars have vertical tangents, govern the reactions of heterogeneous systems of practical interest: these points generally show the equilibria of interaction, dissociation and decomposition of the various condensed phases to which the diagrams refer; and such a region in a diagram which would be of no practical interest in a binary diagram (for example, carbon-oxygen) can become of interest if the superposition of another binary diagram (zinc-oxygen) modifies the isobars in such a way that they show vertical tangents in the ternary diagram (zinc-carbon-oxygen).

(c) MATHEMATICAL FORMULATION OF THE ISOBARS AND OF THEIR TANGENTS CONDITIONS UNDER WHICH THESE TANGENTS ARE HORIZONTAL OR VERTICAL.

Let us consider two reactions

$$O_2 + n_1B_1 + \Sigma \nu_1M_1 = 0$$

$$\text{and } O_2 + n_2B_2 + \Sigma \nu_2M_2 = 0$$

in each of which gaseous diatomic oxygen, O_2, a gaseous substance B_1 or B_2 and condensed substances M_1 or M_2 take part.

The thermodynamical conditions for equilibrium in these reactions are:

$$\log p_{O_2} = \frac{A_1}{T} + B_1 - n_1 \log p_{B_1} \quad . \quad . \quad . \quad . \quad (1)$$

$$\log p_{O_2} = \frac{A_2}{T} + B_2 - n_2 \log p_{B_2} \quad . \quad (2)$$

Denoting the total pressure by P,

$$P = p_{B_1} + p_{B_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

then from (1), the expression for the isobar relating to this pressure P,

$$\log p_{O_2} = \frac{A_1}{T} + B_1 - n_1 \log (P - p_{B_2}), \quad . \quad (4)$$

follows, and from (2), the expression for p_{B_2},

$$p_{B_2} = \left(p_{O_2} \times 10^{-\frac{A_2}{T} - B_2}\right)^{-\frac{1}{n_2}}, \quad . \quad . \quad . \quad . \quad (5)$$

is obtained.

Substituting for p_{B_2} in (4),

$$\log p_{O_2} = \frac{A_1}{T} + B_1 - n_1 \log \left[P - \left(p_{O_2}\, 10^{-\frac{A_2}{T} - B_2}\right)^{-\frac{1}{n_2}}\right] \quad . \quad (6)$$

which is the general equation of the isobars of pressure P.

To obtain the equations of the tangents of these curves, this is differentiated with respect of $1/T$, i.e,

$$\frac{d \log p_{O_2}}{d\, 1/T} = A_1 - n_1 \frac{\frac{1}{n_2}\left[\left(p_{O_2} . 10^{-\frac{A_2}{T} - B_2}\right)^{-\frac{1+n_2}{n_2}} . \left(\frac{d\, p_{O_2}}{d\, 1/T} . 10^{-\frac{A_2}{T} - B_2} - A_2 . p_{O_2} . 10^{-\frac{A_2}{T} - B_2} \log_e 10\right)\right]}{\left[P - \left(p_{O_2} . 10^{-\frac{A_2}{T} - B_2}\right)^{-\frac{1}{n_2}}\right] \log_e 10} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Now, since $$d \log p_{O_2} = \frac{d\, p_{O_2}}{p_{O_2}} . \frac{1}{\log_e 10},$$

then $$d\, p_{O_2} = p_{O_2}\, d \log p_{O_2} . \log_e 10.$$

Substituting d p_{O_2} in (7) then

$$\frac{d \log p_{O_2}}{d\, 1/T} = A_1 - \frac{n_1}{n_2} . \frac{\left(p_{O_2} . 10^{-\frac{A_2}{T} - B_2}\right)^{-\frac{1}{n_2}} . \left(\frac{d \log p_{O_2}}{d\, 1/T} - A_2\right)}{P - \left(p_{O_2} . 10^{-\frac{A_2}{T} - B_2}\right)^{-\frac{1}{n_2}}}$$

or

$$\frac{\mathrm{d}\log p_{O_2}}{\mathrm{d}\ 1/T} = A_1 - \frac{n_1}{n_2} \cdot \frac{\dfrac{\mathrm{d}\log p_{O_2}}{\mathrm{d}\ 1/T} - A_2}{P \left(p_{O_2} \,.\, 10^{-\frac{A_2}{T} - B_2} \right.}$$

or, by expanding $\dfrac{\mathrm{d}\log p_{O_2}}{\mathrm{d}\ 1/T}$,

$$\frac{\mathrm{d}\log p_{O_2}}{\mathrm{d}\ 1/T} = \frac{n_2 A_1 P \left(p_{O_2} \ 10^{-\frac{A_2}{T} - B_2} \right)^{\frac{1}{n_2}} - n_2 A_1 - n_1 A_2}{n_2 P \left(p_{O_2} \ 10^{-\frac{A_2}{T} - B_2} \right)^{\frac{1}{n_2}} - n_2 + n_1} \quad . \qquad (8)$$

which is the general equation for the tangents of the isobars of pressure P

By means of (3) and (5) this may be written as

$$\frac{\mathrm{d}\log p_{O_2}}{\mathrm{d}\ 1/T} = \frac{n_2 A_1 \dfrac{p_{B_1} + p_{B_2}}{p_{B_2}} - n_2 A_1 - n_1 A_2}{n_2 \dfrac{p_{B_1} + p_{B_2}}{p_{B_2}} - n_2 - n_1}$$

or

$$\frac{\mathrm{d}\log p_{O_2}}{\mathrm{d}\ 1/T} = \frac{n_2 A_1 p_{B_1} + n_1 A_2 p_{B_2}}{n_2 p_{B_1} + n_1 p_{B_2}} .$$

We have finally

$$\frac{\mathrm{d}\log p_{O_2}}{\mathrm{d}\ 1/T} = \frac{\dfrac{A_1 p_{B_1}}{n_1} + \dfrac{A_2 p_{B_2}}{n_2}}{\dfrac{p_{B_1}}{n_1} + \dfrac{p_{B_2}}{n_2}} \quad . \qquad (9)$$

which represents, as does (8), the general equation of the tangents of the isobars for the pressure $p_{B_1} + p_{B_2}$, where p_{B_1} and p_{B_2} are the partial pressures of the two gaseous substances taking part in the two reactions considered ; and n_1 and n_2 are the " stoichiometrical coefficients " with which these two gaseous substances take part in the reactions as written above. A_1 and A_2 are related to the heat contents of these two reactions by :

$$\Delta H_1 = -4{\cdot}575\, A_1$$
$$\Delta H_2 = -4{\cdot}575\, A_2$$

Where there are considered not two, but any number of reactions, (9) may be written in the form :

$$\frac{\mathrm{d}\log p_{O_2}}{\mathrm{d}\ 1/T} = \frac{\sum \dfrac{A\,.\,p_B}{n}}{\sum \dfrac{p_B}{n}} \quad . \qquad (10)$$

From this equation, (11) and (12), which express the conditions under which the tangents to the isobars will be horizontal and vertical respectively, are obtained.

Thus, for horizontal tangents,

$$\sum \frac{A\, p_B}{n} = 0 \quad . \qquad . \qquad (11)$$

or, since $\Delta H = -4{\cdot}575\, A$

$$\sum \frac{\Delta H\, p_B}{n} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \qquad (11^1)$$

This equation states that the partial pressures p_B of the reacting gases have values such that the total heat content of reaction is zero.

EXAMPLES.—(1) In the case of the *carbon-oxygen* system, the equation of the locus of the points in the diagram at which the isobars have horizontal tangents may be obtained by applying eqn. (11) to the three following equilibrium equations:

$$0 = \frac{42{,}960}{T} - 8\cdot02 + \log p_{C(g)} \qquad \text{(Reaction C}(s) = \text{C}(g)\text{)}$$

$$0 = \frac{49{,}350}{T} - 8\cdot98 + \log p_{C_2(g)} \qquad \text{(Reaction 2C}(s) = \text{C}_2(g)\text{)}$$

$$\log p_{O_2} = -\frac{11{,}200}{T} - 9\cdot64 + 2\log p_{CO} \qquad \text{(Reaction 2C}(s) + \text{O}_2 = \text{2CO)}$$

From these equations it follows that

$$\left(5600\,.\,10^{\frac{5600}{T}+4\cdot82} \times \sqrt{p_{O_2}}\right) - \left(49{,}350\,.\,10^{-\frac{49{,}350}{T}-8\cdot98}\right) - \left(42{,}960\,.\,10^{-\frac{42{,}960}{T}+8\cdot02}\right) = 0$$

which, expressed as a function of $\log p_{O_2}$ and $1/T$, may be written:

$$\log p_{O_2} = 2\log\left[\left(7\cdot672\,.\,10^{-\frac{48{,}560}{T}+3\cdot20}\right) + \left(8\cdot812\,.\,10^{-\frac{54{,}950}{T}+4\cdot16}\right)\right] \quad . \quad (j)$$

This is the equation of a curve j, drawn in Fig. 5, which is the locus of points at which the tangents of the isobars are horizontal. The curve j has two asymptotes whose equations are respectively:

$$\log p_{O_2} = -\frac{97{,}120}{T} + 8\cdot17 \quad . \quad . \quad . \quad . \quad (k)$$

and

$$\log p_{O_2} = -\frac{109{,}900}{T} + 10\cdot21 \quad . \quad . \quad . \quad . \quad (l)$$

(2) In the case of the *zinc-carbon-oxygen* system the equation of the locus of points at which the isobars have horizontal tangents may be obtained by applying eqn. (11) to the three following equations:

$$\log p_{O_2} = -\frac{48{,}520}{T} + 20\cdot90 - 2\log p_{Zn} \qquad \text{(Reaction 2Zn + O}_2 = \text{2ZnO}(s)$$

$$\log p_{O_2} = -\frac{20{,}280}{T} - 0\cdot34 + \log p_{CO_2} \qquad \text{(Reaction C}(s) + \text{O}_2 = \text{CO}_2\text{)}$$

$$\log p_{O_2} = -\frac{11{,}200}{T} - 9\cdot54 + 2\log p_{CO} \qquad \text{(Reaction 2C}(s) + \text{O}_2 = \text{2CO)}$$

Because of the complexity of the expression which results from these equations, the determination of the locus of points at which the isobars have horizontal tangents is performed graphically on the basis of the equation:

$$24{,}260\, p_{Zn} = 20{,}280\, p_{CO_2} + 5600\, p_{CO}$$

giving curve s of Fig. 6.

For the tangents of the isobars to be vertical, it follows from (10) that

$$\sum \frac{p_B}{n} = 0 \quad . \quad . \quad . \quad . \quad . \quad (12)$$

This equation states that the partial pressures p_B of the gaseous reactants have values such that the total quantity of oxygen involved in the group of reactions

$$O_2 + n_1\,B_1 + \nu_1\,M_1 = 0$$
$$O_2 + n_2\,B_2 + \nu_2\,M_2 = 0$$

is zero.

The group of reactions which can take place is thus accomplished without the transference of oxygen or any other substance to, or from, its surroundings: i.e., the reacting system is a "closed" one.

Two examples have been given above of the application of this equation to the particular systems zinc-oxygen and zinc-carbon-oxygen. In Fig. 4 and 5 which represent portions of the diagrams relating to the equilibria of these two systems, the loci of the points at which the tangents of the isobars are vertical are shown by curves *g* and *m*.

The Phase Rule

The variance of the physico-chemical systems whose equilibria are represented by the diagrams discussed above can be deduced by simple examination of these diagrams and by the application of the following rule :—

All curves in the diagrams correspond to a *univariant* system, except when they are affected by a parameter involving the values of the partial pressures (or concentrations) of two substances other than diatomic oxygen O_2 ; in this case the system is *bivariant*.

As a result of this (apart from the few curves which are affected by such a parameter) :—

A *point* corresponds to an *invariant* system, a *curve* to a *univariant* system and a *group of curves* to a *bivariant* system; and for the lines which are affected by such a parameter, a *point* corresponds to a *univariant* system, a curve to a *bivariant* system and a *group of curves* to a *trivariant* system.

A proof of this rule which holds good for any number of constituents in the system is given below.

The number of degrees of freedom, v, of a physico-chemical system may be calculated from the following relation deduced by De Donder [14] :

$$v = c - r + 2 - \varphi$$

where c is the number of independent reacting components,

r is the number of independent chemical reactions,

φ is the number of phases.

Since the equilibrium conditions of all reactions have been expressed in the form

$$\log p_{O_2} = f(1/T) - \Sigma n \log p_B$$

where p_B denotes the partial pressures of the gaseous components other than diatomic oxygen, O_2 (or the concentration of a substance in solution), which eventually take part in the reaction. Each of the curves, which denote the characteristics of the equilibria of these reactions, is relative to a fixed value of the function, $\Sigma n \log p_{O_2}$ considered as a parameter, or, in the case of an isobar, to a given value of the total pressure

$$P = p_{O_2} + \Sigma p_B .$$

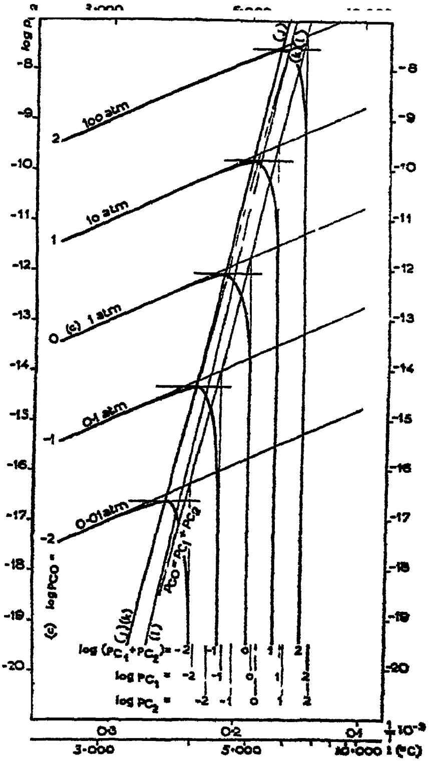

FIG. 5.—Carbon-oxygen equilibrium (detail).

As this is the case, it is possible to calculate the variance of the system of which the equilibrium characteristics are represented in the diagrams : thus if
a is the number of condensed substances not in solution taking part in the reaction, and

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[14] De Donder, van den Dungen and van Lerberghe, *Leçons de thermodynamique et de chimie physique* (Paris, 1920).

b is the number of gaseous (and dissolved) substances of which the partial pressures (or concentrations) appear in the function $\Sigma n \log p_B$ of the reaction equation,

then, for each of the reactions, the different reacting components are those substances belonging to the two groups just considered, and diatomic gaseous oxygen O_2. The number c of these reacting components is thus given by

$$c = a + b + 1$$

The *phases* are those which constitute the different non-dissolved condensed phases and the gas phase. The number of phases Q is given by

$$Q = a + 1.$$

Finally, for each reaction,

$$r = 1.$$

The number of degrees of freedom of each of the systems is thus given by

$$v = (a + b + 1) - 1 + 2 - (a + 1),$$

whence

$$v = b + 1.$$

It follows from this that:—

(1) A system in which a reaction occurs without involving a dissolved or a gaseous substance, apart from diatomic oxygen, O_2* (and for which $b = 0$) is univariant.

(2) A system in which a reaction takes place involving *one* dissolved or *one* gaseous substance other than O_2 is bivariant.

(3) A system in which a reaction takes place involving *two* dissolved or *two* gaseous substances other than O_2, is trivariant.

Since the conditions of equilibrium are represented in the first of these three cases by a curve, they are represented in the other two cases by groups of curves; each curve of these groups relates to a fixed value of a parameter and thus represents the loss of a degree of freedom, the system thus produced has therefore a variance diminished by one unit. Thus, except in the third case, all the curves in the diagram represent a univariant equilibrium; in the third case they represent a bivariant equilibrium.

EXAMPLES.—(1) In Fig. 1 (*zinc-oxygen* system there is no curve in which the function relates to two substances, and thus every curve in this figure represents an univariant equilibrium. At any particular temperature each of the systems depicted is completely fixed.

Curve *d* represents the *univariant* equilibrium, $ZnO(s) - Zn(l) - O_2(g)$. The group of curves *e* represents the bivariant equilibrium $ZnO(s) - Zn(g) - O_2(g)$, which becomes univariant for each member of the group of curves (for which p_{Zn} is constant). Thus for curve *g*, relating to the thermal decomposition of $ZnO(s)$ (for which the condition $p_{Zn} = 2p_{O_2}$ reduces by one the variance of the system) and for the isobars (for each of which the condition, $p_{Zn} + p_{O_2} =$ constant, has been imposed).

In Fig 1, the invariant equilibrium, $Zn(s) = Zn(l)$ is represented not by a point, but by a curve. This produces results in the system $Zn(s) - Zn(l) - O_2(g)$ being *univariant*, because it is possible for $Zn(s)$ and $Zn(l)$ to coexist at various oxygen pressures.

In the top right-hand corner of Fig. 1 is a group of curves which are related to the homogeneous, bivariant, one component system $O_2(g) - O(g)$; each curve of this group represents a system made univariant by the fact that a fixed value of p_O has been imposed; at any point on these lines the system is invariant and fixed with respect to the temperature, p_{O_2} and p_O.

(2) In Fig. 2 (*carbon-oxygen* system) the lines of group *e* contain a function in which two substances other than O_2, namely CO and CO_2 play a part. The system represented by this group of lines is thus trivariant. Each of these lines, relating to a fixed p_{CO_2}/p_{CO} ratio represents a bivariant system (e.g., the system $CO_2 - CO - O_2$ in which the temperature and one other property, e.g., $P = p_{CO} + p_{CO_2}$ are independently variable). Every point on these lines

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* It should be remembered that owing to the principle on which these diagrams were constructed, O_2 is present in *all* the physico-chemical systems considered.

represents a univariant system (e.g., *P* is variable) except that if another condition is imposed, such as the coexistence of solid carbon, it becomes invariant. The system is then fixed, and the total pressure and the partial pressures of CO_2 and CO have definite values which may be read on the diagram.

(3) In Fig. 3 (*zinc-carbon-oxygen* system) the part of the group of isobars (for which $CO_2 + CO + Zn = P =$ constant) which lie in the region where solid ZnO and solid C are mutually stable corresponds to the bivariant system, $ZnO(s) - C(s) - (CO_2 + CO + Zn(g) + O_2)$. On each of those isobars the system is univariant; at any temperature there is a fixed value of the partial pressure of each of the gases. If an additional condition is imposed on the system, it becomes invariant, and is then represented by a point. Thus, in the presence of solid $ZnCO_3$, the system is represented by the point of intersection of the isobar and curve *d*; in the presence of liquid Zn it is represented by the intersection of the isobar with curve *c*; in the presence of an atmosphere in which the partial pressure of CO and Zn(*g*) are equal, the system is represented by the intersection of the isobar and the curve *m*.

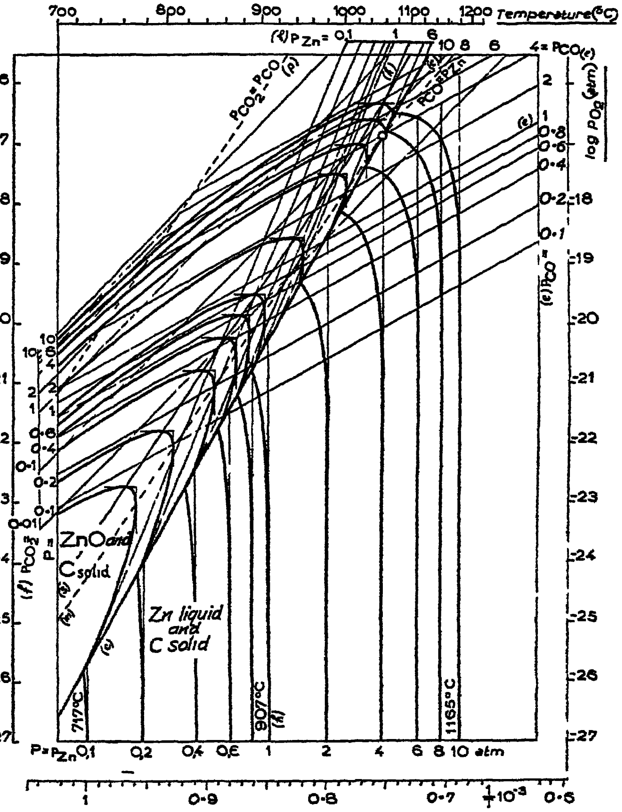

FIG. 6.—Zinc-carbon-oxygen equilibrium (detail).

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Summary

An examination is made of some properties of the diagrams of complex equilibria constructed by plotting the inverse of the absolute temperature as abscissa and the

logarithm of the equilibrium oxygen pressures of all the transformations which can occur in the system as ordinate.

At all points in these diagrams the slope of the *tangents* of the isobars are a measure of the quotient Q/n, where Q is the heat content change of the sum of all the reactions simultaneously possible, and n the number of g. mol. oxygen needed by the system for these reactions.

At the points where these tangents are *horizontal*, the total heat content of the reaction is zero: the quantities of substances taking part in the various reactions are such that the sum of the heat evolved by the exothermic reactions is equal to that absorbed by the endothermic reactions.

At the points where these tangents are *vertical*, the sum of the reactions occurs without the exchange of oxygen with the surroundings of the system: the quantities of substances taking part in the various reactions are such that the quantity of oxygen liberated by the reduction reactions is equal to that combining in the oxidation reactions; it is particularly at these points where the tangents are vertical that the heterogeneous systems of practical interest are represented.

The variance of the physico-chemical systems whose equilibrium characteristics are represented in these diagrams can readily be deduced from a rapid examination of them.

A few examples are given from the systems: zinc-oxygen, carbon-oxygen and zinc-carbon-oxygen.

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STUDIES IN THE THERMODYNAMICS OF METALLURGICAL REDUCTION PROCESSES BY ELECTROCHEMICAL METHODS

By B. A. Rose, G. J. Davis and H. J. T. Ellingham

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For any chemical reaction or other reversible process which tends to occur spontaneously at any specified constant temperature and pressure and which can be " harnessed " as a voltaic cell, the electromotive force, E, of the cell at that temperature and pressure, and its temperature coefficient, $\partial E/\partial T$, at constant pressure in the neighbouring temperature range, are directly related to the principal thermodynamic characteristics of the reaction under the specified conditions. Thus,

$$-\Delta G = nFE$$

$$\Delta S = nF \, . \, \partial E/\partial T$$

$$-\Delta H = -\Delta G - T.\Delta S = nFE - nFT \, . \, \partial E/\partial T$$

where, for n g.-equivalents of chemical change under the given conditions, $-\Delta G$ (the decrease in the Gibbs function, G) is the free energy of the reaction, a measure of its " driving force " or tendency to occur spontaneously; ΔS is the increase of entropy accompanying the process; $-\Delta H$ is the heat of reaction—the heat evolved when the unharnessed process occurs: F is Faraday's constant, 96,500 coulombs/g. equivalent, and, with E expressed in volts, the values of the above quantities will be in joules.

Moreover, if all the substances participating in the reaction are at unit activity—each solid or liquid substance being present as a separate pure phase or as a saturated solution, and each gaseous substance (behaving as an ideal gas) at a partial pressure of 1 atm. —, the quantities E, $-\Delta G$,

ΔS and $-\Delta H$ will have their " standard " values E°, $-\Delta G^\circ$, ΔS° and $-\Delta H^\circ$ for the specified temperature and

$$nFE^\circ \equiv -\Delta G^\circ = RT \ln K$$

where R is the gas constant per g.-molecule (8·315 joules) and K the equilibrium constant of the reaction at that temperature.

The simplicity of these relations and the fact that measurements of the E.M.F. of cells at various temperatures can be readily made with considerable accuracy renders such measurements particularly attractive for the determination of thermodynamic data for reactions that can be harnessed in this way, especially as by the use of cells with molten salt electrolytes the measurements can be made up to any desired temperature. Moreover, in as much as for many reactions $\partial E/\partial T$ and hence ΔS, and $-\Delta H$ are sensibly constant over a wide range of temperature so long as all the participating substances remain in the same physical state, the temperature at which any change of physical state occurs is indicated by an abrupt alteration in the slope of the practically linear $E - T$ curve, and $nFT \,.\, \Delta(\partial E/\partial T)$ at that point is the latent heat (in joules) of the change.

Again, for a voltaic cell that behaves reversibly, the minimum voltage that must be applied from an external source in order to reverse the cell reaction is identical with the E.M.F., and measurement of such reversible decomposition voltages provides an alternative method for determining thermodynamic data which is sometimes convenient though generally much less accurate.

For the study of the thermodynamics of reduction and oxidation processes of metallurgical interest, over temperature ranges used in practice, several types of voltaic cells are available and have received some attention from this point of view. Thus, cells of the Daniell type with molten (or solid) salts, especially molten halides, as electrolytes, e.g., $M \mid MCl_2 \vdots M'Cl_2 \mid M'$, have been extensively studied by Lorenz and his collaborators.[1-5] The cell reaction being $M' + MCl_2 = M + M'Cl_2$, the displacement of one metal by another, the E.M.F. of the cell at a given temperature, if corrected for any potential at the junction of the two salts, would give the difference between the free energies of formation of those salts at that temperature. Unfortunately, little is known about the magnitudes of liquid junction potentials between molten or solid salts in general, and the absence of activity and mobility data for the relevant ions precludes even their approximate assessment. There is good evidence that such liquid junction potentials between chlorides of similar metals are negligible [3-5] but it is not certain how far this extends to salts of somewhat different types. This limitation is avoided by the use of cells with a single electrolyte, such as $M \mid MCl_2 \mid Cl_2$, also studied by Lorenz and others, and, with special reference to the activities of components of salt mixtures, by Hildebrand and his co-workers[6-9]; or $M \mid MO$, molten salt $\mid O_2$ largely investigated, especially by Baur and collaborators,[10] in the course of work on fuel cells. Although the E.M.F. of these cells may provide a direct measure of the free energy of formation of chlorides, oxides, etc., other

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[1] Lorenz and Kaufler, *Elektrochemie geschmolzener Salze* (1909)
[2] Lorenz and Oppenheimer, *Z. anorg. Chem.*, 1927, **161**, 183.
[3] Lorenz and Michael, *Z. physik. Chem. A*, 1928, **137**, 1.
[4] Lorenz and Velde, *Z. anorg. Chem.*, 1929, **183**, 81.
[5] Oppenheimer, *Z. anorg. Chem.*, 1930, **189**, 297.
[6] Hildebrand and Rule, *J. Amer. Chem. Soc.*, 1927, **49**, 722.
[7] Salstrom and Hildebrand, *J. Amer. Chem. Soc.*, 1930, **52**, 4641.
[8] Wachter and Hildebrand, *J. Amer. Chem. Soc.*, 1930, **52**, 4655.
[9] Salstrom, *J. Amer. Chem. Soc.*, 1934, **56**, 1272.
[10] Baur and Tobler, *Z. Elektrochem.*, 1933, **39**, 169 (summary of work on fuel cells); Baur and Brunner, *Z. Elektrochem.*, 1935, **41**, 794; 1937, **43**, 725.

difficulties enter, notably in obtaining reliable gas electrodes, especially for oxygen. The work of Treadwell, Ammann and Zürrer[11] on cells giving the free energy of formation of magnesium oxide affords, however, a good example of the successful application of this method to oxides.

In measurements of the decomposition voltage of such molten salt systems the question of providing a gas electrode does not arise but considerable uncertainties enter in the necessary extrapolation of voltage data to zero current. The work of Cuthbertson and Waddington[12] on the decomposition voltage of alumina dissolved in molten cryolite, using a platinum anode, shows, however, that this method can be usefully applied.

The accuracy of direct measurements of E.M.F., as well as of decomposition voltage, on systems involving molten metals and salts may also be seriously affected by the tendency of the metal to disperse in the melt forming a "metal fog".[13] In some systems hydrolysis of salts through traces of moisture may also introduce notable errors (see below).

One of the main purposes of the present investigations, carried out at the Imperial College in 1936–40, was to explore the possibilities of electrochemical measurements of the above types in furnishing data of metallurgical interest, with special reference to the influence of various factors on their accuracy and reproducibility. E.M.F. or decomposition voltage measurements were made on a variety of systems that might give information on the reducibility of representative halides, oxides and sulphides at temperatures up to 1000° K.

Experimental

Cells were set up in an electric furnace consisting of a section of iron pipe, coated externally with an insulating layer of asbestos paper on which was wound Nichrome wire with an external coating of asbestos paper, the whole being placed vertically in an iron canister filled with sand. This simple type of furnace proved entirely satisfactory for temperatures up to 1000° K, particularly as the use of the heavy iron pipe ensured uniformity of temperature in the interior over a considerable length. Where the leads from the electrodes of a cell to the exterior of the furnace were of different metals, the thermo-E.M.F. arising was determined by direct measurement and the apparent E.M.F. of the cell corrected accordingly: the greatest values of this correction (at 1000° K.) were 0·0112 v. for silver/graphite and 0·0158 v. for silver/nickel.

Reducibility of Halides

(EXPERIMENTAL WORK BY B. A. ROSE)

Measurements were made of the E.M.F. of the following cells over ranges of temperature up to 1000° K.:—

A + Ag | AgCl | $PbCl_2$ | Pb
B + Ag | AgI ¦ AgCl ¦ $PbCl_2$ Pb
C, C′ + Ag | AgCl ¦ $SnCl_2$ Sn
D + Ag | AgI ¦ AgCl ¦ $SnCl_2$ Sn
E + Sn | $SnCl_2$ ¦ $PbCl_2$ Pb
F ± Ag | AgCl ¦ AgI Ag

and the results are shown on an *E–T* diagram in Fig. 1, with reference letters as above. Points determined by Lorenz and co-workers for cells A and E are shown by open circles: for cell A they agree reasonably well with those obtained in the present work, but for cell E they are too scattered to afford a basis of comparison. Similar irregularities were observed by the present authors in some preliminary measurements, especially on cells with stannous chloride half-elements, and were no doubt due, at least in part, to hydrolysis of the salt through the presence of moisture. In order to eliminate moisture that might enter during the filling of such cells, Salstrom and Hildebrand [7] adopted the practice of passing a stream of dry hydrogen chloride through the molten salt,

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[11] *Helv. chim. Acta*, 1936, **19**, 225.
[12] *Trans. Faraday Soc.*, 1936, **32**, 745
[13] Karpatschov and Poltoratska, *J. Physic. Chem.*, 1936, **40**, 763; Drossbach, *Trans. Electrochem. Soc.*, 1936, **70** (preprint 18).

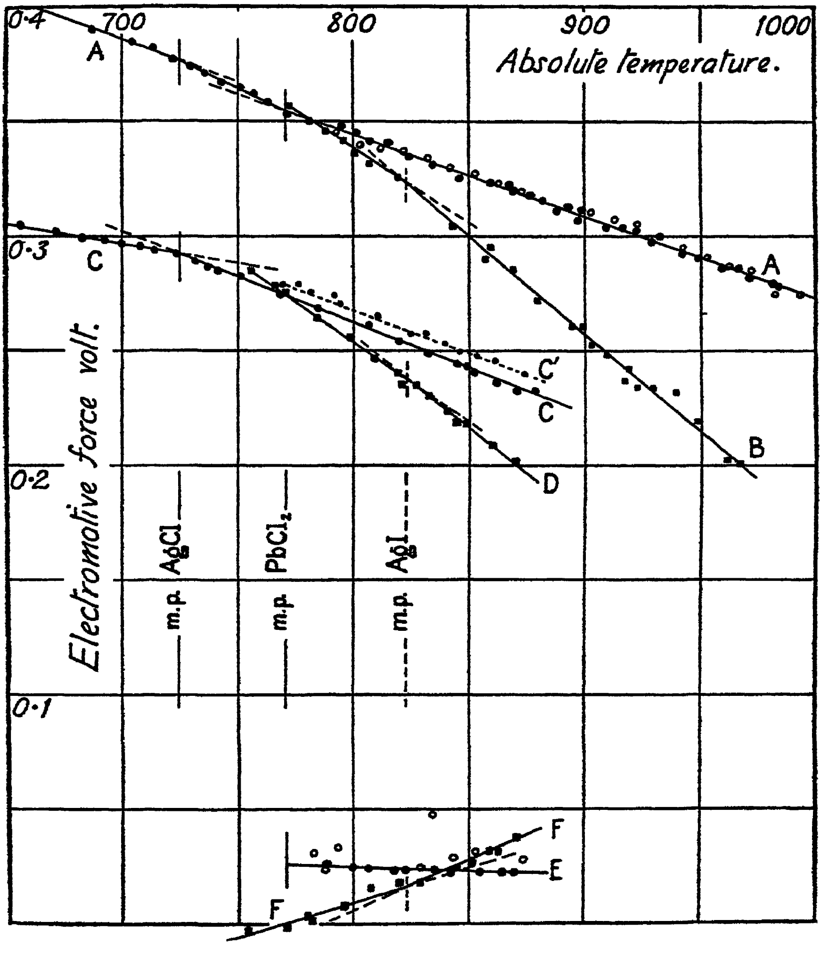

FIG. 1.

and it was found that this procedure, generally maintained after the cells were set up, greatly improved the reproducibility and consistency of the results. This improvement may be due in part to the action of HCl in preventing formation of metal fog, for lead chloride in cells where this treatment was applied was found to remain white whereas otherwise it became black. The data represented in Fig. 1 were all obtained after the passage of HCl through $PbCl_2$, as well as $SnCl_2$, melts had been adopted as a regular practice, using specially designed electrode vessels of Pyrex glass illustrated in Fig. 2. The consistency of the results thus obtained for cell E, as compared with those of Lorenz and Oppenheimer,[8] is satisfactory though the absolute accuracy of measurements of cells with $SnCl_2$ half-elements may still not be very high, as is indicated by the discrepancy between values for cell C in separate investigations (lines C and C′)

At any temperature above the melting points of lead chloride and stannous chloride, substitution of the half-element Ag | AgI ¦ AgCl for Ag | AgCl in cells A and C produces substantially the same change in E.M.F., which agrees well with the E.M.F. of cell F, e g.,

	E_A–E_B	E_C–E_D	$E_{C'}$–E_D	E_F
at 850° K.	0·027	0·029	0·032	0·028

On the other hand, while the difference in E.M.F. of similar cells with Pb | $PbCl_2$ and Sn | $SnCl_2$ half-elements is satisfactorily constant, this difference is by no means equal to the E.M.F. of cell E, e.g.,

	E_A–E_C	E_B–E_D	E_E
at 800° K.	0·083	0·085	0·025
at 850° K.	0·081	0·083	0·023

Lorenz and Michael,[3] from their discordant values for cell E, reported that E_E was about 0·031 V. at 773° K. It must be concluded that the difference between the junction potentials for AgCl ¦ $PbCl_2$ and AgCl ¦ $SnCl_2$ differs notably from that for $PbCl_2$ ¦ $SnCl_2$, presumably because of the unequal extent of some specific interaction of AgCl with $PbCl_2$ and $SnCl_2$, due perhaps to $Sn^{\cdot\cdot}$ ions having a greater tendency than $Pb^{\cdot\cdot}$ ions to form complex anions in the presence of Ag ions.

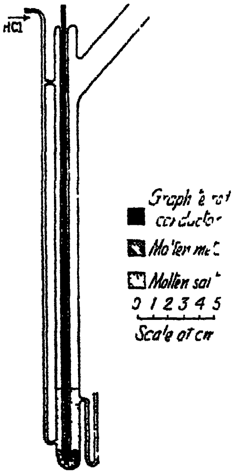

FIG. 2.

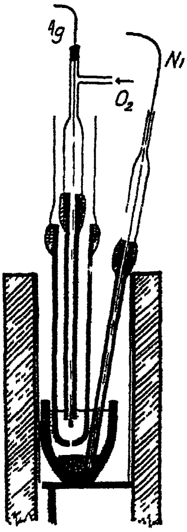

FIG. 3.

As the E.M.F. of a cell with two or more electrolytes is determined not only by the electrode reactions but also by the tendency of the electrolytes to mix irreversibly, the values of thermodynamic quantities derived from it may also differ notably from those appertaining to the simple metal displacement process, and the possibility of specific interactions occurring to diverse extents at salt junctions introduces a further uncertainty in the interpretation of such data. Nevertheless, the effects of these factors on ΔS and $-\Delta H$ are probably much smaller than on E and $-\Delta G$, and "apparent" values of the former quantities obtained in this way, such as those given below for the temperature range 775–1000° K. may be useful as approximate data in connection with metallurgical processes involving molten halides.

Cell:	A	B	C	D	E	F
$-\Delta H$ (kcal./g.-equivt.)	14·54	23·50	13·42	21·88	1·17	− 8·03

For the displacement of tin by lead, A − C gives 1·12, in good agreement with 1·17 from cell E; the notably higher figure, 1·62, from B − D may be due, at least in part, to uncertainty in the slope of curve B, for the points are abnormally scattered at higher temperatures.

In Fig. 1 the temperature at which the E.M.F. of cell F changes sign is about 770° K., while those at which curves A and B and curves C and D intersect (which should be the same) are 780° and 772° K. respectively. Melting points given by changes in the direction of the lines are 725° K. for AgCl (lines A and C), 771° K. for $PbCl_2$ (line A) and about 820° K. for AgI (lines B, D, F). From the change of slope of curve C at 725° K. the latent heat of fusion of AgCl comes out as 3·15 kcal./g.-equivt. (22·0 cal./g.). Measurements were not continued far enough below the melting points of the other salts to permit determination of their latent heats of fusion with reasonable accuracy.

It is concluded that reasonably reproducible values for the E.M.F. of Daniell cells with molten halide electrolytes can be readily obtained if due precautions are taken to prevent hydrolysis of salts such as stannous chloride and to minimise metal fog formation, and that, although liquid junction potentials may not always be negligible, their magnitude can often be estimated from differences in the E.M.F. of cells in which one half-element is varied. From the results of such measurements over a sufficiently wide range of temperature useful data for heats of reaction and latent heats of fusion, as well as for free energies of reaction, can be determined with sufficient accuracy for many practical purposes. Extension of the method to cells with salts of other types and to complex melts involved in specific metallurgical processes, might well afford the simplest means of obtaining such data.

Reducibility of Oxides

(EXPERIMENTAL WORK BY B. A. ROSE AND G. J. DAVIS)

In recent years increasingly accurate data for the free energy and heat of formation of metal oxides at temperatures used in smelting operations have been obtained, largely from thermal measurements, by various investigators, notably by Chipman and his collaborators. Critical examinations of such data have been made by Kelley [14] and later, more completely, by Thompson.[15] The value of a general $(-\Delta G)$–T (or E–T) diagram in indicating the conditions under which the oxides of the various metals can be reduced by particular reducing agents, including other metals, has been shown by Ellingham.[16]

Much remains to be done, however, not only in obtaining still more accurate values of free energies, especially at higher temperatures, but also in determining the effect of varying the concentration of an oxide when it is present as an unsaturated solution in a molten system, a condition commonly met with in practice. In the present work the possibility of investigating such effects by E.M.F. measurements has been explored using solutions of stannic oxide and of plumbous oxide in molten caustic soda.

The cells employed were:

A $+ O_2$ (Ag or Pt) | NaOH, SnO_2 | Sn
B $+ O_2$ (Ag) | NaOH, PbO | Pb

They were set up in the form shown in Fig. 3 using "recrystallised alumina, ΔRR" (Morgan Crucible Co.) as the material of the containing vessel and the oxygen electrode tube. Direct experiment had shown that this material, which is free from siliceous bonding material, was not appreciably attacked by molten caustic soda under the conditions of the investigation; at 900° K. the loss was only about 0·0015 g.cm.$^{-2}$ hr.$^{-1}$. The same material was used for the perforated tube surrounding the oxygen electrode (Fig. 3); for cell B this tube contained only caustic soda so as to minimise possible errors due to oxidation of PbO.

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[14] *U.S. Bur. Mines Bull.*, 1932, and onwards.

[15] *The Total and Free Energies of Formation o the Oxides of Thirty-two Metals* (The Electrochemical Society, 1942).

[16] *J. Soc. Chem. Ind.*, 1944, 63, 125.

The results are shown in Fig. 4. Those for cell A refer to stannate melts in which the mole fraction of SnO_2 (determined by analysis of the solidified material after use) was (*a*) 0·0096, (*b*) 0·0126, (*c*) 0·0316, (*d*) 0·023; in cells (*a*) and (*c*) the oxygen electrode was set up with platinum as intermediary whereas in cells (*b*) and (*d*), investigated at a later date, silver was used. The plumbite melt contained a small but undetermined concentration of PbO. The lines marked SnO_2, SnO and PbO represent, in terms of E.M.F., the most probable values of the standard free energy of formation of these oxides derived from the equations given by Thompson.[15] The small difference between these values of E° for the formation of SnO_2 and SnO (e.g., 0·0209 v. at 800° K.) indicates that in a melt a notable proportion of SnO_2 tends to be converted to SnO in the presence of tin. This does not affect the proposition that if an indifferent melt were fully saturated with SnO_2 the E.M.F. should correspond with the standard free energy of formation of SnO_2 at the given temperature. The same applies to melts saturated with PbO, though in this case the corresponding equilibrium with PbO_2 lies well over on the side of PbO.

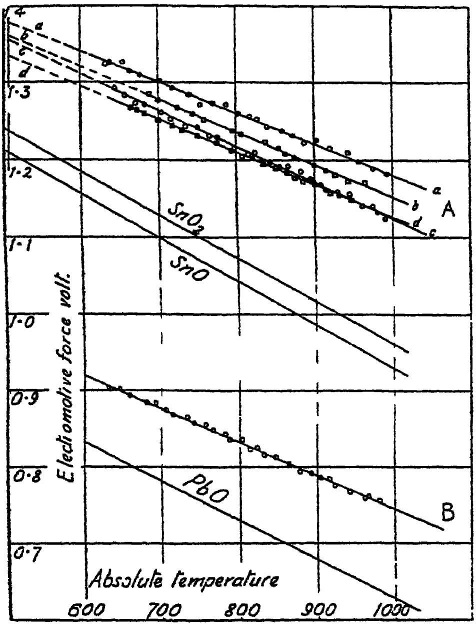

FIG. 4.

The relative positions of the lines A (*a–d*) and the SnO_2 line show that decreasing the concentration of SnO_2 in the melt raises the E.M.F. of cell A, as is to be expected, though the higher E.M.F. values at most temperatures for A*c* as compared with A*d* indicate that the accuracy and reproducibility are not sufficient to show the effect of small differences in concentration. More concentrated solutions were too viscous to be used in a cell with an oxygen electrode and it was not practicable, therefore, to obtain lines nearer to that for SnO_2. The wide gap between the lines for cell A and that for SnO_2 corresponds to a very low activity of SnO_2 in the melts employed, as would be expected from the tin being present essentially in the form of complex anions with only an extremely small effective concentration of the $Sn^{\cdot\cdot\,\cdot\cdot}$ ions which presumably determine the potential of the tin electrode. On the other hand, in the presence of excess caustic soda, ions that determine the potential of the oxygen electrode probably have a much higher effective concentration than if they were derived solely from the stannic oxide, thus making the E.M.F. lower than it would be in an indifferent solvent that did not furnish such ions. Preliminary experiments with similar cells with ZnO and CdO in molten caustic soda gave E.M.F. values that were actually slightly less than those derived from the $-\Delta G^\circ$ data for the pure oxides, so that it is clear that more information is required before activity data can be deduced from such measurements. Nevertheless, the E.M.F. values should reflect the extent to which oxides become increasingly difficult to reduce as their concentration in molten caustic soda is diminished, and are thus of direct practical significance for reduction processes in such systems. Also, the results for SnO_2 may give some indication of the probable behaviour of SiO_2 in similar systems; thus, a comparable lowering of the activity of free silica in a $MgO–SiO_2$ system with excess of MgO would support the explanation given[16] for the relatively low temperatures required for the reduction of MgO by silicon (or ferro-silicon).

Interest also attaches to the effect of dissolution on the heat of reaction: values derived from the lines in Fig. 4 are as follows:

Cell:	A (*a*)	A (*b*)	A (*c*)	A (*d*)	SnO_2
$-\Delta H$ (kcal./g.-equivt.)	36·3	36·4	36·5	35·7	$-\Delta H^\circ = 34{\cdot}8$

Cell:	B	PbO
$-\Delta H$ (kcal./g.-equivt.)	27·4	$-\Delta H^\circ = 26{\cdot}2$

The difference between a value of $-\Delta H$ and the corresponding standard value, $-\Delta H^\circ$, should represent the heat of dissolution of the oxide in the corresponding melt.

Reducibility of Sulphides

(EXPERIMENTAL WORK BY G. J. DAVIS)

The free energies of formation of a number of metal sulphides over a wide range of temperature have been collected by Kelley [17] and the most probable $(-\Delta G^\circ)$–T relations set forth. These data have been represented on a $(-\Delta G)$–T diagram by Ellingham[16] so as to indicate the relative reducibility of the various sulphides at any temperature.

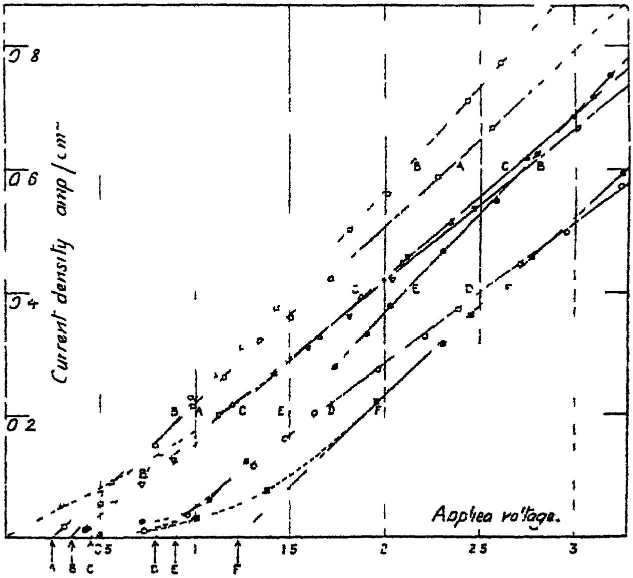

FIG. 5.

The fact that many sulphides of the heavy metals dissolve to a notable extent in the molten halides of the same or certain other metals, and that electrolysis of such melts liberates metal at the cathode and may yield gaseous sulphur at the anode, suggests the possibility of obtaining approximate free energies of formation of sulphides from decomposition voltage measurements. Moreover, as the electrolysis of lead sulphide dissolved in molten lead chloride has been proposed[18] as a means of extracting lead direct from sulphide ores with recovery of sulphur as a by-product, the extension of decomposition voltage measurements to practical current densities is also of interest in showing the voltage, and hence the energy requirement, for the electrolysis of this and similar melts at various temperatures and current densities.

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[17] *U.S. Bur. Mines Bull.*, No. 406, 1937.

[18] Richardson, *Bull. Inst. Min. Met.*, No. 387, 1936; Newall, *Trans. Inst. Chem. Eng.*, 1938, **16**, 96.

Typical current density–applied voltage curves obtained by electrolysis of sulphide-halide melts and of pure molten AgCl and $PbCl_2$, with graphite plates as electrodes, in the temperature range 550°–600° c. are shown in Fig. 5. As in all such measurements, uncertainties enter in the extrapolation of the curves to zero current, for such curves are not in general strictly rectilinear or strictly logarithmic ; also small traces of more easily liberated impurities can greatly distort the curves at the lower current densities. In systems of this particular type there may be other sources of error : thus, nothing is known about the conditions for anodic liberation of gaseous sulphur—the extent of any polarisation or even if the process is completely reversible under these conditions. Again, it is possible that these sulphide-halide systems may not be wholly electrolytic conductors ; some degree of electronic conduction is possible.

Results obtained with pure halide melts give some confidence, however, in the assumption that the curves can be regarded as straight lines above a small current density (say, 0·2 amp/cm ^{2}), for extrapolation on this basis gives 1·23 v. for $PbCl_2$ at 550° c. (curve F) and 0·89 v. for AgCl at 560° c (curve E), the former being in good agreement with the value, 1·24 v., obtained by Wachter and Hildebrand[8] by a direct E.M.F. measurement and the latter with 0·90 v. obtained by combining this with the present authors' measurement of the E.M.F. of the cell $Ag \mid AgCl \vdots PbCl_2 \mid Pb$.

The following decomposition voltages were obtained for the specified sulphide melts and are compared with E.M.F. values corresponding to free energies of formation of the sulphides at the same temperature, derived from the equations presented by Kelley.

Curve in Fig. 5	Sulphide	Solvent	g. sulphide per 100 g solvent	Temperature c.	Decomposition voltage observed	from $-\Delta G$
—	Bi_2S_3	$PbCl_2$	2	550	0·12	0·22
A	Sb_2S_3	$PbCl_2$	3	572	0·25	0·24
B	Ag_2S	$PbCl_2$	2	530	0·34	0·30
B′	Ag_2S	AgCl	5	550	0·35	0·30
—	SnS	$PbCl_2$	5	590	0·40	—
—	SnS	$PbCl_2$	5	600	0·40	—
C	PbS	$PbCl_2$	2	590	0·44	0·45
—	CdS	$CdCl_2$	5	600	0·57	0·67
D	ZnS	$ZnCl_2 + CaCl_2$	5	550	0·78	0·82

Measurements made on Cu_2S, CdS and ZnS in $PbCl_2$ gave values corresponding to PbS, showing that these sulphides were less easily decomposed than PbS. ZnS was only very slightly soluble in $PbCl_2$ and at a moderate current density the voltage for decomposition of PbS jumped suddenly to that for $PbCl_2$ in the customary manner when one electrode process gives place to another. Even in $ZnCl_2$ very little ZnS dissolved and $CaCl_2$ was, therefore, added to increase the solubility.

Although these determinations are admittedly of a preliminary nature and the solutions used were of varying degrees of saturation, it is satisfactory to find that (*a*) a particular sulphide gives practically the same value in different solvents, and (*b*) the sequence of the sulphides in order of increasing decomposition voltages is the same as that in order of increasing free energies of formation. A closer agreement between observed and calculated decomposition voltages could probably not be expected under the conditions of these measurements and in view of possible disturbances due to formation of stable complexes and to some degree of electronic conduction.

The results indicate, however, that this very simple method, which could readily be applied over a wide range of temperature, might be developed to give data for the free energy of formation of sulphides of sufficient accuracy for many approximate metallurgical calculations. Moreover, the values so obtained refer to the actual systems used and require no correction for the activities of the substances concerned, quantities which can be obtained only from special investigations on individual systems such as have recently been instituted by Anderson.[19]

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[19] Anderson and Ridge, *Trans. Faraday Soc.*, 1943, 39, 93, 98.

THE PRIMARY REACTIONS IN ROASTING AND REDUCTION PROCESSES

By J. S. Anderson

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Processes of roasting and reduction of metallic ores are, in general, heterogeneous reactions of the type

$$A_{\text{solid}} + B_{\text{gas}} \rightarrow C_{\text{solid}} + D_{\text{gas}}$$

The detailed mechanism of reactions of this kind—as indeed of all reactions of solids—is, as yet, imperfectly understood, and it is therefore of interest to review the information which may be derived from as many lines of evidence as possible. In so far as the adequate sojourn of a gas molecule upon the surface of the solid reactant is a prerequisite for the occurrence of reaction, it is apparent that the first act in the chemical process must involve chemisorption. Studies by Garner and his co-workers[1] of the adsorption of reducing gases (H_2 or CO) and of their oxidation products (H_2O or CO_2) upon the surface of metallic oxides have contributed substantially to our present understanding of the mechanism of reduction processes.

When a molecule of hydrogen or of carbon monoxide is chemisorbed on a metal oxide, it is, as pointed out by Garner, presumably bound as 2 OH^- ions or a CO_3^{2-} ion respectively, by interaction with oxide anions of the surface. In either case, additional valence electrons must be accommodated in the crystal lattice, and may be bound by lowering the valence of one or more cations. Similarly, in oxidation processes, the chemisorption of oxygen withdraws electrons from the crystal lattice, generally by raising the valence of an appropriate number of cations. The localised excess electrons and positive holes, created respectively in these two processes, constitute impurity centres which confer electronic conductivity on the solid compound, since at temperatures above 0° K. a proportion of the electrons or positive holes, determined by some Boltzmann factor $e^{-E/RT}$, is mobile. The chemisorption of oxygen or hydrogen therefore confers semi-conducting properties on the substrate, and information derived from studies of semi-conductivity can be useful to supplement that based on adsorption, especially as the relevant measurement can be made over the temperature range at which reduction processes or roast reactions become significant. This paper summarises some evidence derived from studies of semi-conduction in oxide and sulphide systems, carried out at the University of Melbourne, and for the most part already published.[2]

The Reduction of Metallic Oxides

The literature relating to the semi-conducting properties of metal oxides is extensive,[3] but the general behaviour of compounds of this type is adequately summed up by the so-called Friederich-Meyer rule.[4] This states that the electronic conductivity of those oxides derived from the highest valence state of the metal (e.g., ZnO, TiO_2) is increased when the partial pressure of oxygen, in contact with the oxide at elevated temperatures, is diminished; conversely, for oxides derived from the lower of two accessible valence states (e.g., NiO, Cu_2O), diminution of oxygen pressure diminishes the electronic conductivity.

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[1] *J. Chem. Soc.*, 1947, 1239.

[2] (*a*) Anderson and Morton, *Proc. Roy. Soc. A*, 1945, **184**, 83; (*b*) Anderson and Morton, *Trans. Faraday Soc.*, 1947, **43**, 185; (*c*) Morton, *Trans. Faraday Soc.*, 1947, **43**, 194; (*d*) Anderson, Bevan and Shelton, *J. Chem. Soc.* (in press); (*e*) Anderson and Bevan (unpublished).

[3] See, for example, Gudden, *Erg. exak. Naturwiss*, 1934, **13**, 222; Wagner *et al.*, *Z. physik. Chem. B*, 1932, **17**, 467; 1933, **22**, 199, 212; 1934, **24**, 59; 1936, **32**, 439; Meyer, *Physik. Z.*, 1936; ref. 2 (*d*); Mott and Gurney, *Electronic Processes in Ionic Crystals* (Oxford, 1940).

These empirical regularities find their interpretation in the statistical-thermodynamical model of the solid state, developed by Schottky and Wagner.[5] At temperatures above the absolute zero, the free energy of a stoichiometric crystal is a minimum when a certain proportion of positive and negative ions is displaced from proper lattice positions, so that there are either (*a*) equal concentrations of vacant cation and anion sites, or (*b*) interstitial ions of one kind and an equal number of vacant sites. The stoichiometric compound is, however, a special case; for the more general case of an ionic compound in equilibrium with one of its components—e.g., an oxide MO in the presence of oxygen, at temperatures where equilibrium can be attained—we must consider the possibility of adding or removing O^{2-} ions at the surface of the originally stoichiometric crystal by the processes (I) or (II).

(I) $2M^{2+} \rightarrow 2M^{3+} + 2e$
$\frac{1}{2}O_2 + 2e \rightarrow O^{2-}$ (on lattice site) + cation hole.

(II) $O^{2-} + M^{2+}$ (both on lattice sites) $\rightarrow \frac{1}{2}O_2$ (gas) + M^{2+} (interstitial) + $2e$ (trapped near interstitial atom).

Process (II), by the ionisation of the trapped electrons, confers electronic conductivity on the resulting oxide; process (I) confers positive hole conduction. Any change in the partial pressure of oxygen shifts the equilibria of processes (I) or (II), and thereby changes the conductivity in the manner already summarised in the Friederich-Meyer rule.

In true equilibrium, lattice defects within the interior of the crystal lattice may be regarded as distributed at random. The free-energy change associated with the production of a lattice defect in the surface atom layer is, however, different from that of a defect remote from the surface; hence the equilibrium concentration of defects at the surface will differ from that of the crystal lattice as a whole, and the extent to which a minute deviation from ideal composition can result from change in the oxygen pressure above a metallic oxide is, to some extent, dependent on the specific surface of the solid. Moreover, interaction of the solid with the gas phase creates defects at the surface; to attain true equilibrium these must be transferred to the interior of the crystal by a diffusion process. Diffusion in ionic solids is associated with high activation energy, and first reaches significant magnitudes at temperatures around or above $0{\cdot}5\ T_m$,[6] (T_m = melting point of the crystal on absolute scale). Phenomena occurring at markedly lower temperatures can reasonably be regarded as involving the surface atom layers only.

Recent work by Shelton, Bevan and the author[2 (d)] on the conductivity of some simple oxides (ZnO, Fe_2O_3, Cr_2O_3) and spinel-type double oxides ($ZnFe_2O_4$, $ZnCr_2O_4$) provides evidence as to the interaction between the solid oxide phase and the ambient gas phase. In this work, the resistance of fritted plates of the oxides was measured at temperatures up to 1000°, in oxygen pressures between 1 atm. and 10^{-4} mm. and (with Cr_2O_3 and $ZnCr_2O_4$)

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[4] Friederich, *Z. Physik*, 1925, **31**, 813; Meyer, *Z. Physik*, 1933, **85**, 278.
[5] *Z. physik. Chem. B*, 1930, **11**, 163.
[6] Tammann, *Z. anorg. Chem.*, 1925, **149**, 67.

in reducing atmospheres of hydrogen or carbon monoxide. The experimental details are fully reported in the reference cited and are, therefore, not recapitulated here. The type of conduction exhibited by these oxides accorded with expectations based on the Friederich-Meyer rule, as follows from the data summarised in Fig. 1. ZnO, Fe_2O_3 and $ZnFe_2O_4$ are metal-excess, electronic conductors, whilst Cr_2O_3 and $ZnCr_2O_4$ are oxygen-excess, positive hole conductors under all conditions, even when treated with hydrogen or carbon monoxide at high temperatures. It would, therefore, appear that a small stoichiometric excess of oxygen is invariably contained in the structure of these latter compounds.

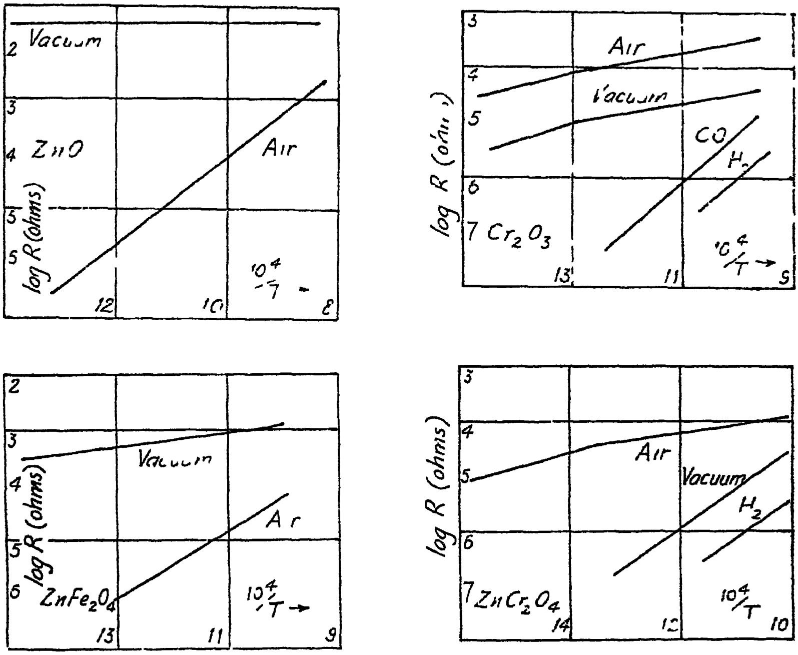

FIG. 1.—Conductivity changes of oxides in oxidising and reducing conditions.

Observations on the conditions under which the oxides could be equilibrated with the gaseous atmosphere, and the rate at which equilibrium is attained, are relevant to the present discussion of the mechanism of reduction, and may be summarised as follows.

(i) The conductivity of metal oxides, in every instance examined, responds rapidly to changes in oxygen pressure, even at temperatures below the Tammann temperature. Thus, with $ZnCr_2O_4$, the resistance of a plate at 520°, after treatment with hydrogen, fell immediately from $1{\cdot}6 \times 10^6$ ohms to $3{\cdot}5 \times 10^4$ ohms; after 2 hr. in oxygen the resistance had assumed a final value of 2×10^4 ohms. At 760° the potential-leads to the same plate were connected to an oscilloscope; the movement of the trace resulting from admission of oxygen, evacuation, or admission of hydrogen, was sensibly perpendicular to the time axis. The melting point of $ZnCr_2O_4$ has not been recorded, but from that of Cr_2O_3 (1990° C.), and by analogy with $ZnFe_2O_4$ (m.p. 1590°) and Fe_2O_3 (1565°) it can hardly be much lower than 1900° C. Hence it is improbable that processes occurring rapidly at temperatures much lower than *ca.* 820° C. can involve inner diffusion. Similarly, with zinc oxide (m p. 2100° C.) the resistance at 500° ($= 0{\cdot}32\ T_m$) changed on exposure to a vacuum ($p_{O_2} > 10^{-4}$ mm.) from 10^6 ohms to 100 ohms during 4 hr. These observations were made on oxides which had been ignited and subsequently fritted into plates at 1000°–1100° for prolonged periods, during which considerable grain growth and recrystallisation must have occurred. A rough estimate of the self-diffusion coefficient based on Braun's and the Langmuir-Dushman approximation sets the mean diffusion path at 500° in 4 hr. as of the order of a few A., indicating that defects created at this temperature are effectively confined to the surface.

We infer, accordingly, that the process changing the semi-conducting properties by alteration of the stoichiometric metal-oxygen rates, in the experiment cited, was a surface reaction. It is significant that the work of Jander [7] and of Huttig [8] on solid-solid reactions and on the fritting process should point to the onset of processes involving bulk-phase diffusion only above a reduced temperature of $0{\cdot}5\ T_m$, but of surface changes at about $0{\cdot}3\ T_m$. The latter corresponds well to the reduced temperature above which we have found the semi-conducting properties of oxides to display ready reversibility.

(ii) The rapid process occurring at the surface is followed by migration of lattice defects into the crystal lattice. The total concentration of impurity centres thereby rises slowly, since the surface equilibrium is maintained, and the diffusion process may be observed as a slower drift of conductivity, following the initial rapid change that accompanies alterations in oxygen pressure. With zinc chromite, which appears invariably to deviate somewhat from ideal stoichiometric composition (oxygen excess), the slow second process is marked.

(iii) The conductivity of Cr_2O_3 and of $ZnCr_2O_4$ was determined in the presence of carbon monoxide and of electrolytic hydrogen, containing approximately 0·1 % oxygen; the latter was not removed, as by its combustion a constant H_2/H_2O ratio was maintained in the gas. The equivalent partial pressure of oxygen $\left(= K_{H_2O}\left(\frac{p_{H_2O}}{p_{H_2}}\right)^{2}\right)$ in such an atmosphere is independent of the total pressure, so that if the primary process in the reduction of the surface were the evaporation of oxygen from the lattice (Fig. 2, IIA)—as does take place in vacuum—the resulting conductivity should be independent of the hydrogen pressure. Fig. 3 summarises two sets of preliminary measurements on $ZnCr_2O_4$ in hydrogen at 735°. The diminution in concentration of positive holes as the hydrogen pressure is increased clearly indicates a pressure-dependent adsorption equilibrium, creating new lattice defects (in this case annulling positive holes already present) by the mechanisms IIB, IIC respectively; the evaporation of H_2O or CO_2 from the surface then occurs as a subsequent stage in reduction. An identical mechanism brings about the creation of negative holes on the surface of oxides displaying metal-excess conduction (e.g., ZnO, Fe_2O_3). This work therefore substantiates at temperatures where reduction processes take place, the mechanism deduced from Garner's studies of adsorption on active oxides at lower temperatures.[1] [9]

We can, accordingly, recognise three stages in the process of reduction of a metallic oxide to the metal phase.

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[7] cf. Jander and Herrmann, *Z. anorg. Chem*, 1939, **241**, 225.

[8] cf. Huttig, *Angew. Chem.*, 1936, **49**, 882; *Kolloid Z*, 1941, **97**, 281; 1942, **98**, 6, 263.

[9] See also Gel'd and Esin, *Bull. Acad Sci. U.R.S.S.*, 1946, 899; *Brit. Abstr.*, 1947, **41**, 2311.

STAGE I. A SURFACE PROCESS—chemisorption of the reducing gas, whereby lattice defects are created at the surface. This initial act proceeds at relatively low temperatures, and becomes rapid at temperatures appreciably above 0·3 T_m. Garner's work shows that two partial processes may be involved in this stage; some support for this view is discussed below in relation to the primary roasting reaction on sulphide surfaces.

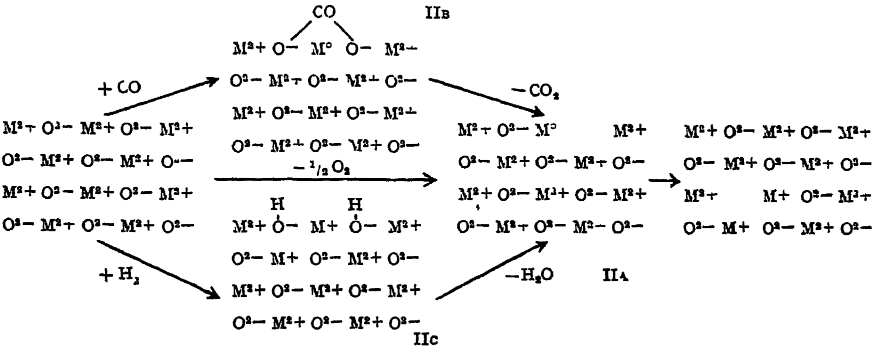

FIG. 2.

STAGE II. MIGRATION OF LATTICE DEFECTS FROM THE SURFACE—a process dependent on the attainment of a sufficiently high diffusion coefficient, and therefore of importance at temperatures above 0·5 T_m.

STAGE III. SATURATION OF THE CRYSTAL LATTICE WITH DEFECTS, with consequent appearance of a new phase (i.e., metal or a lower oxide). The measurements of semi-conductivity establish the fact that deviations from ideal stoichiometric composition are produced in the reduction process; general experience makes it evident that most crystal structures have only a small tolerance for departures from ideal composition. The simple statistical-thermodynamic model is strictly valid only when defects are present in high dilution.[5, 10]

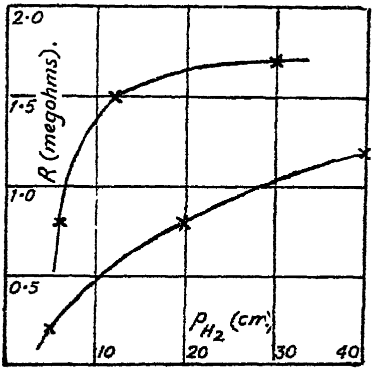

FIG. 3.—Conductivity of $ZnCr_2O_4$ in hydrogen.

Few experimental studies have been made of this third stage. Some results recently obtained[2(e)] on the conductivity of zinc oxide under low oxygen pressure appear to have some bearing on the nucleation of the new phase under conditions where reaction is restricted to a surface process. Experimental data, and a fuller discussion of the results will be presented elsewhere; reference is made here to certain aspects relevant to the present theme.

The evaporation of oxygen from the crystal lattice of zinc oxide may be represented by the equilibria

$$Zn^{2+}\ (l) + O^{2+}\ (l) \rightleftharpoons \tfrac{1}{2}O_2 + \underbrace{Zn^{2+} + 2e} \qquad . \quad . \quad (1)$$

$$\text{Trapped electron} \rightleftharpoons \text{free electron} + \text{ion} \qquad . \quad . \quad (2)$$

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[10] Anderson, *Proc. Roy. Soc. A*, 1946, 185, 69.

where $\mathrm{Zn}^{2+}(l)$, $\mathrm{O}^{2-}(l)$ represent ions on proper lattice sites, and the location of the resulting zinc atom (i.e., an ion + trapped electron) is open to discussion. Von Baumbach and Wagner[11] consider that the excess zinc is accommodated interstitially, and that the electrons are trapped in the neighbourhood of the interstitial ions.

Then from (1),

$$[\mathrm{Zn}(i)] = k_1 . p_{\mathrm{O}_2}^{-1/2} \quad . \quad . \quad . \quad . \quad (3)$$

and from (2), if only a small proportion of the trapped electrons are freed thermally,

$$[\mathrm{Zn}^{2+}(i)]\,[e]^2 = k_2[\mathrm{Zn}(i)], \text{ and } [e] = 2[\mathrm{Zn}^{2+}(i)],$$

$$\text{so that } [e] = k_3 . p_{\mathrm{O}_2}^{-1/6}. \quad . \quad . \quad . \quad . \quad (4)$$

If, on the other hand, the electrons may be trapped at any positive ion in the crystal,

$$[e] = k_3' . p_{\mathrm{O}_2}^{-1/4} \quad . \quad . \quad . \quad . \quad (5)$$

Von Baumbach and Wagner measured the conductivity $\varkappa$ of zinc oxide at two temperatures (550° and 600°) and over a very restricted pressure range (10–800 mm. of oxygen), and found

$$\varkappa = C . p_{\mathrm{O}_2}^{-\frac{1}{4\cdot 3}} \quad . \quad . \quad . \quad . \quad (6)$$

By using a flow of oxygen or of (99 % N_2 + 1 % O_2)-mixture through a variable leak system, we have been able to maintain oxygen pressures between 1 atm. and 10^{-6} mm., and have measured the conductivity of zinc oxide under these controlled conditions at temperatures up to 800°. Some results are summarised in Fig. 4. At oxygen pressures from 1 atm. down to 10^{-2} — 10^{-3} mm., the conductivity follows the relation $\varkappa \propto p^{1/n}$, the mean value of n being approximately 4·3 as found by von Baumbach and Wagner; there is some indication of a trend from higher to lower values of n with rise of temperature.

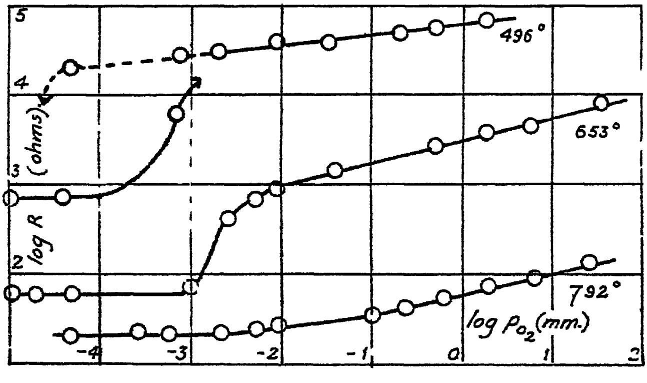

FIG. 4.—Conductivity of ZnO against oxygen pressure.

At very low oxygen pressures (10^{-4} — 10^{-5} mm.) the conductivity becomes practically independent of oxygen pressure, indicating that the equilibrium of eqn. (1) to (4) or (5) no longer solely determines the concentration of conduction electrons.

At high temperatures (e.g., 800°) there is a smooth transition from the state where (5) is approximately valid (p_{O_2}>0·1 mm.) to that where $\varkappa$ is independent of pressure ($p_{O_2} < 10^{-3}$ mm). At low temperatures, there is a discontinuous transition, when the oxygen pressure is reduced below some limit p_c, the conductivity rises to its pressure-independent value. This discontinuous increase of conductivity is a slow process; careful equilibrium measurements show that the course of the curve is quite reversible, but that hysteresis loops are readily obtained at those lower temperatures (e.g., 500°) where attainment of equilibrium is slow. On the linear portion of the log p — log $\varkappa$ curve, including the metastable portion ($p < p_c$), response of conductivity to change of oxygen pressure is much more rapid, even at 500°. The magnitude of the step in the log p — log $\varkappa$ curve diminishes progressively, and is displaced towards slightly higher pressures as the temperature is raised.

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[11] *Z. physik. Chem. B*, 1933, **22**, 199.

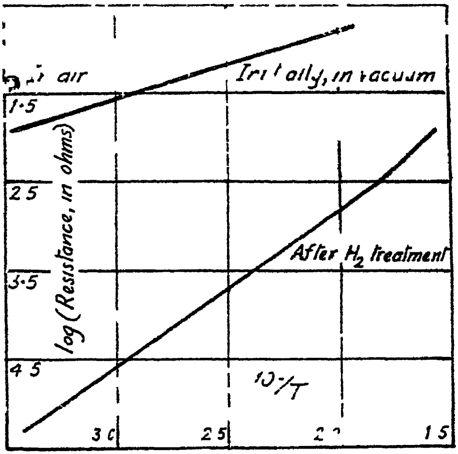

FIG. 5.—Conductivity of SnS in oxidising and reducing conditions.

That the maintenance of equilibrium in reaction (1) is much faster than the process responsible for the step, suggests that this reflects the operation of a diffusion process. Furthermore, since this process occurs with moderate speed at a temperature as low as 500° (0·32 T_m), a surface diffusion process, or one involving at the most the superficial atom layers, rather than diffusion within the crystal lattice, appears to be indicated. This process sets in when the surface concentration of lattice defects rises sufficiently. As p_c does not vary greatly with temperature, whereas the extent to which the surface is stripped varies for constant p_{O_2} according to some exponential factor $e^{-E/kT}$, the requisite concentration of defects apparently increases with temperature.

It cannot be assumed that the phenomenon represents the complete dissociation of zinc oxide and the separation of metallic zinc, for from the free energy data [12] the equilibrium pressure of oxygen is about 10^{-15} mm. at 800° K., and 3×10^{-11} mm. at 1000° K. The interpretation of the facts is, therefore, not yet clear. A tentative hypothesis is that the mutual interaction of lattice defects leads to the formation of an ordered monolayer of zinc atoms on the surface, as envisaged by Fowler.[13] If this is valid, it indicates a stage of 2-dimensional reduction and nucleation preceding the formation of the metallic phase. On this model, as the surface is stripped in increasing degree by direct evaporation of oxygen, or by chemisorption of hydrogen or carbon monoxide, the following successive stages would be traversed

$$\begin{tikzcd}
\text{Stoichiometric oxide} \arrow[r] & \text{Non-stoichiometric oxide with metal excess} \arrow[r] & \text{Nucleation of 2-dimensional metal phase} \arrow[d] \\
& & \text{Metallic phase in bulk.}
\end{tikzcd}$$

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[12] Truesdale and Waring, *J. Amer. Chem. Soc.*, 1941, **63**, 1610.

[13] Fowler, *Proc. Camb. Phil. Soc.*, 1936, **32**, 144; Fowler and Guggenheim, *Statistical Thermodynamics* (Cambridge, 1939), p. 340.

It may be noted that in addition to its role in the complete reduction of oxide to the metal phase, the surface condition obtaining at low oxygen pressures is that which promotes the processes of recrystallisation and fritting in oxide ceramics.

The Roasting of Metallic Sulphides

The previous section has summarised evidence for the formation of stoichiometric imperfections as intermediate stages in the reduction of metal oxides. Formation of markedly non-stoichiometric phases is more general amongst the sulphides of the heavy metal than amongst the oxides.[14] It is, therefore, of some interest to examine the role that such phases play in chemical reactions.

The sulphides of the transition metals proper—e.g., the pyrrhotite FeS phase,[15] cuprous sulphide [16] and silver sulphide [17]—which have a wide composition range, possess moderate or high electronic conductivity. The conductivity varies with composition, but is intrinsically too great to be markedly affected by surface reactions. In stannous sulphide and lead sulphide—also derived from metals of potentially variable valency—the metallic character is much less pronounced and the accessible range of composition much smaller, although for lead sulphide the variability of composition is probably detectable.[18] The stoichiometric compounds have a low electrical conductivity, but an excess of metal or of sulphur converts both into good semi-conductors.

Oxidation of Clean Sulphide Surfaces.—The semi-conducting properties of stannous sulphide have been described previously.[2 (a)] [2 (b)] As prepared, with a slight stoichiometric excess of sulphur, the material is a positive hole conductor with fairly good conductivity ($\varkappa$ *ca.* 0·1–0·01 at 18° c.). When heated in hydrogen at 300°, or when baked in high vacuum for prolonged periods, the conductivity at 18° c. is diminished by a factor of 10^4–10^6; persistence of positive hole conduction (as shown by measurements of thermoelectric effect) indicates that a small stoichiometric excess of sulphur must remain. Stannous sulphide with electronic conductivity—i.e., with a stoichiometric excess of tin—is formed only by rather drastic reduction, or when brought into equilibrium with metallic tin as a separate phase.

Admission of oxygen at the ordinary temperature to such a "reduced" specimen of stannous sulphide instantaneously restores the positive hole conductivity. The conductivity acquired in oxygen is a function of the oxygen pressure (Fig. 6) and at high oxygen pressures may equal or exceed the conductivity of the original sulphur-rich material.

It is evident that at relatively low temperatures oxygen is chemisorbed on to the sulphide surface, being bound as some molecular or atomic oxide ion (see below). As is discussed previously,[2 (a)] [2 (b)] [2 (c)] the conduction characteristics of the resulting "oxy-sulphide" are in no way different from those of the pure sulphide, and it would appear that O^{2-} ions can replace S^{2-} ions in the crystal lattice in appreciable proportion.

Lead sulphide resembles stannous sulphide in essential properties, but the tolerance towards variability in composition is distinctly wider. Hintenberger[19] showed that the semi-conducting properties of evaporated films of lead sulphide could be varied reversibly by exposure to sulphur vapour or by baking in vacuum. The composition may be thereby changed from positive hole conducting (sulphur-rich) material to electron conducting (sulphur-deficient) material. Our own observations indicated that the Pb/S ratio may be altered by upwards of 1 % in this process whilst preserving the homogeneity of the PbS phase.

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[14] cf. *Ann. Reports*, 1946, **43**, 104 *et seq*

[15] Roberts, *J. Amer. Chem. Soc.*, 1935, **57**, 1034; Haraldsen, *Z. anorg. Chem.*, 1937, **231**, 78; 1941, **246**, 169, 195.

[16] Buerger, *J. Chem. Physics*, 1939, **7**, 1067; *Econ. Geol.* 1941, **36**, 19

[17] Reinhold and Schmitt, *Z. physik. Chem. B*, 1939, **44**, 75; Kracek, *Trans. Amer. Geophys. Union*, 1946, **27**, 364.

[18] Ref. 2 (*c*); Schleede and Büggische, *Z. anorg. Chem.*, 1927, **161**, 85; Frey, *Z. Elektrochem.*, 1930, **36**, 511.

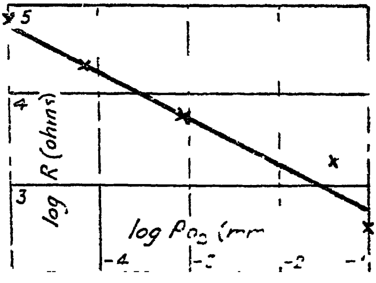

FIG 6.—Conductivity of SnS in oxygen.

On exposure to oxygen, positive hole conducting lead sulphide behaves exactly as does stannous sulphide; chemisorption of oxygen takes place rapidly and fresh positive holes are created. With electron conducting lead sulphide, the first chemisorption of oxygen diminishes the stoichiometric excess of lead, thereby destroying conducting centres and causing an immediate initial fall in conductivity. When the stoichiometric *metal/non-metal* ratio (i.e., S + O) becomes < 1, as the building of oxygen on to the structure continues, the conductivity rises again. Simultaneous measurements of the thermoelectric effect show that this effect changes sign, as the conduction mechanism changes, when the conductivity passes through its minimum value (Fig. 8).

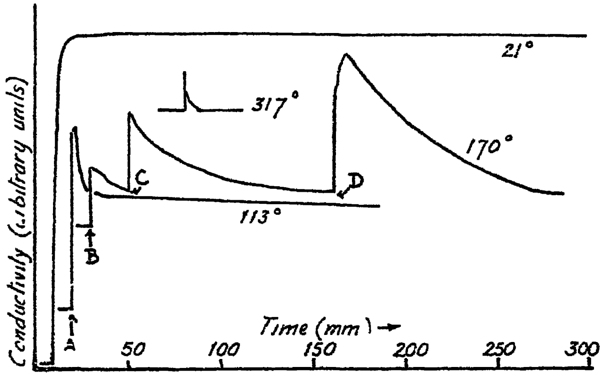

FIG. 7.—Change of conductivity of SnS with time following admission of oxygen.
A — 0·01 mm. O_2 admitted.
B — 0·001 mm. O_2 admitted.
C — 0·002 mm. O_2 admitted.
D — 0·028 mm O_2 admitted.

In the two instances studied, the interaction between a sulphide surface and oxygen conforms to the general pattern established for the reduction process on oxide surfaces. There is some evidence that this is general, in that the oxidation of sulphide minerals (e.g., pyrrhotite) is particularly rapid in the case of those sulphides which deviate markedly from ideal stoichiometric composition. Buerger[16] has suggested that part of the uncertainty attaching to the polymorphism of chalcocite, Cu_2S, arises from the readiness with which oxygen is built on to the crystal structure to give an oxy-sulphide with the symmetry of the digenite phase, $Cu_2S_{1\cdot 11}$.

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[19] *Z. Physik.*, 1942, 119.

Reactions following Chemisorption of Oxygen.—We have observed, in the oxidation of lead sulphide, and especially of stannous sulphide surfaces, progressive changes in the semi-conductivity which can be interpreted as reflecting the course of chemical reactions following the initial step of chemisorption.

The immediate great increase in conductivity observed at room temperatures after admitting oxygen, up to a small partial pressure, to a " reduced " surface is followed, over a period of hours, by a decrease in conductivity. Thus, for SnS pellet IV[2 (a)] at 20° :—

Initial resistance	32,000 ohms
Oxygen (<0·01 mm.) admitted—	
After 30 min. . . .	4,900 ,,
55 ,, . . .	5,160 ,,
120 ,, . . .	5,300 ,,

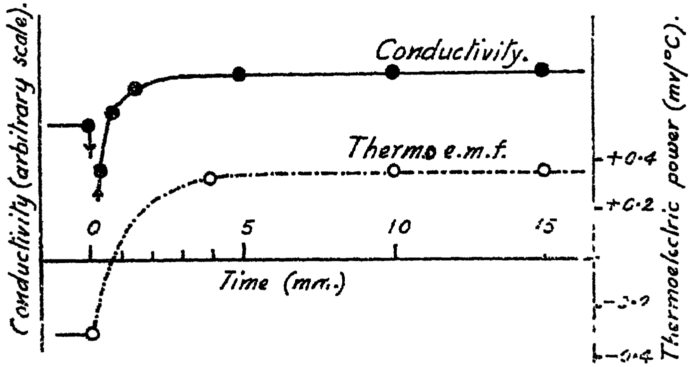

FIG. 8.—Change of conductivity of PbS following admission of oxygen to metal-rich material.

Heating such an oxidised specimen in a " dynamic " vacuum resulted in complete restoration of the " reduced " state. At moderate temperatures the instantaneous creation of positive holes, followed by the slower process in which positive holes are destroyed, can conveniently be observed. It is hoped at some time to make a special study of this phenomena ; some data obtained incidentally in the course of other work are summarised graphically in Fig. 7, in which conductivity is plotted (on an arbitrary scale) as a function of time elapsing after admission of oxygen. At 113° C. the decay of conductivity was measurable but slow ; at 170° the material reverted to its original conductivity in about 120 min. ; at 317° after an initial " flash " of conductivity, the original condition was restored within 5 min. The whole effect is found only when the oxygen pressure is not too high ; i.e., the surface must not be saturated with adsorbed gas.

The effect is not to be ascribed to mere desorption of oxygen, as the decline of conductivity is not reversed on cooling. The oxidation of metal sulphides in air with formation of sulphur oxides proceeds freely at temperatures above 300°, so that it can logically be inferred that oxidation proceeds under the conditions of our experiments. The reversion of the SnS to its original conductivity implied that although the *metal/non-metal* ratio was not permanently changed (no permanent creation of positive holes), the observed reaction represented the partial substitution of O^{2-} for S^{2-} as the prior condition for separation of oxide, etc., as ultimate oxidation products.

We may, furthermore, observe that the data plotted in Fig. 6 accord with the relation: $K = C \cdot p_{O_2}^{1 \cdot 8}$—i.e., approximately 2 positive holes are created per molecule of oxygen chemisorbed. If this interpretation be correct, oxygen is built on to the crystal lattice either as 2 O^- ions per molecule of O_2 added (Fig. 9A) or as molecular O_2^{2-} ions. The chemisorption process is

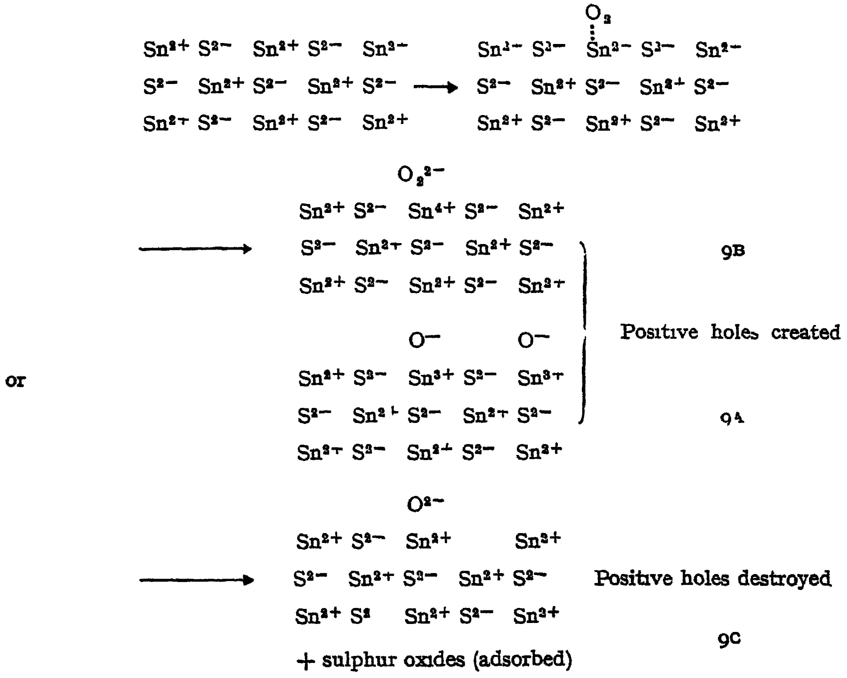

FIG 9

very rapid at room temperature, so that the former process, which would presumably involve the higher activation energy, appears the less likely. (Fig. 9B). This, then, provides a mechanism for the first stage in the roast reaction. Stage 2, which does involve an activation energy and so proceeds with measurable speed at moderately high temperatures, would then be that represented as 9C, in which the positive hole is destroyed, and some oxide of sulphur formed.

Without the performance of work specially directed to this end, the hypothesis developed above must remain purely tentative. It does, however, provide a model for oxidation processes which parallels that developed for reduction reactions.

It may be noted that where (e.g., in roasting PbS) sulphates or basic sulphates are the ultimate product of roasting, these can probably be regarded as secondary products, arising from reactions of sulphur oxides in the adsorption layer.

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A NEW METHOD FOR STUDYING THE MECHANISM OF ROASTING REACTIONS

By E. A. Peretti *

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In the extraction of several of the important non-ferrous metals from their ores, roasting is practised as an intermediate operation, e.g., in the production of copper, lead, zinc and mercury. If we let M represent a divalent metal, the most probable reactions taking place can be generalised as follows:

$$MS_2(s) \rightleftharpoons MS(s) + \tfrac{1}{2}S_2(g) \quad . \quad . \quad . \quad . \quad (1)$$

$$\tfrac{1}{2}S_2(g) + O_2(g) = SO_2(g) \quad . \quad . \quad . \quad . \quad (2)$$

$$MS(s) + 1\tfrac{1}{2}O_2(g) = MO(s) + SO_2(g) \quad . \quad . \quad . \quad (3)$$

$$SO_2(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons SO_3(g) \quad . \quad . \quad . \quad . \quad (4)$$

$$MO(s) + SO_3(g) \rightleftharpoons MSO_4(s) \quad . \quad . \quad . \quad (5)$$

$$MSO_4(s) \rightleftharpoons MO \,.\, ySO_3(s) + (1 - y)\,SO_3(g) \quad . \quad . \quad (6)$$

$$MO \,.\, ySO_3(s) \rightleftharpoons MO(s) + ySO_3(g) \quad . \quad . \quad . \quad (7)$$

At the temperatures commonly used for roasting, reactions (2) and (3) for the metals mentioned possess such large free-energy changes that the SO_2/O_2 equilibrium ratios need not be considered. For example, by using FeS in reaction (3) a thermodynamic calculation results in the following (nomenclature of Lewis and Randall [1]):

$$\Delta F^\circ = -113{,}000 + 9{\cdot}5T \log T - 1{\cdot}965 \times 10^{-3}T^2 - 6{\cdot}7T \quad . \quad (8)$$

and at 1100° K. the equilibrium constant, K, is $1{\cdot}12 \times 10^{18}$. Kelley's [2] standard free-energy equation for reaction (2) yields a K of $2{\cdot}76 \times 10^{18}$ at 1100° K. This means, then, that at these temperatures for eqn. (2) and (3) the oxide and sulphur dioxide will be the stable phases in the presence of even small amounts of oxygen. On the other hand, the thermodynamics of (4), (5), (6) and (7) are such that the temperature and the partial pressure of sulphur trioxide determine which of the solid phases are stable. The respective equilibrium constants are

$$K_4 = \frac{f_{SO_3}}{f_{SO_2} \times \sqrt{f_{O_2}}} \quad . \quad . \quad . \quad . \quad (9)$$

$$K_5 = \frac{1}{f_{SO_3}} \quad . \quad . \quad . \quad . \quad . \quad (10)$$

$$K_6 = f_{SO_3}^{(1-y)} \quad . \quad . \quad . \quad . \quad . \quad (11)$$

$$K_7 = f_{SO_3}^{y} \quad . \quad . \quad . \quad . \quad . \quad (12)$$

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[1] Lewis and Randall, *Thermodynamics* (McGraw-Hill Book Company, 1923).

[2] Kelley, *U.S. Bur. Mines*, Bull. 406, 1937, 13.

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Applying the phase rule[3] we find that a system in which SO_2, O_2, SO_3, MO, MSO_4 and MO . ySO_3 are in equilibrium is nonvariant, and this will be at the point where

$$f_{SO_3} = K_4 \cdot f_{SO_2} \cdot \sqrt{f_{O_2}} = \frac{1}{K_5} = K_6^{\left(\frac{1}{1-y}\right)} = K_7^{\frac{1}{y}} \quad . \quad . \quad (13)$$

For the coexistence of gas and (*a*) MSO_4 and MO, (*b*) MSO_4 and MO . ySO_3, (*c*) MO and MO . ySO_3, the systems are univariant.

There are two degrees of freedom for the stability of gas and any single solid phase. The solid will be :

(*a*) MSO_4, if $f_{SO_3} > \frac{1}{K_5}$ and $> K_6^{\left(\frac{1}{1-y}\right)}$,

(*b*) MO, if $f_{SO_3} < \frac{1}{K_5}$ and $< K_7^{\frac{1}{y}}$

and (*c*) MO . ySO_3, if $f_{SO_3} < K_6^{\left(\frac{1}{1-y}\right)}$ and $> K_7^{\frac{1}{y}}$.

If the roasting operation is carried out under non-equilibrium or changing conditions, which is probably the actual case most of the time, the solid phases present in an industrial calcine may be determined largely by the rate of the various reactions and the mechanisms by which they proceed. Of the seven general reactions listed, all but two are of the heterogeneous solid-gas type for which the mechanism is difficult to determine by the methods usually used for homogeneous reactions because diffusion of gases to and from the reaction interface is very often the rate-controlling factor.

Roasting experiments are usually performed by heating an extremely large number of small particles in a stream of gas. As a result it is almost impossible to analyse an individual piece to determine the sequence of phase formation. The employment of a single lump of mineral is discouraging because of the difficulty of cutting many specimens to a given size and shape and because of the tendency to cracking. It is believed that the technique to be described overcomes these objections.

Experimental

As an example, let us consider the roasting of CuS. Relatively pure specimens of the mineral can be obtained or an artificially prepared compound can be used ; we chose the latter, Fisher's C P. cupric sulphide, which was all minus 100 mesh. Forty-seven grams of the sulphide were placed in a steel mould and made into a cylindrical briquette under a pressure of 3500 lb. in.$^{-2}$. The compresses measured 2·86 cm diam. by 2·86 cm. long and had sufficient strength to be handled without breaking. From three to five of the briquettes were placed in an electrically-heated muffle furnace whose temperature was automatically controlled to within ± 5° C. of the desired value. The specimens were successively removed from the furnace at varying time-intervals and allowed to cool under a graphite crucible.

The course of the reaction was followed by cutting the reacted cylinders in half, transversely, and measuring the diameters of the visible phase boundaries. In less than a minute after the cylinders were placed in the furnace, sulphur gas was liberated, which burned at the surface with its characteristic flame. As long as these flames were visible only two solid phases, CuS and Cu_2S, existed in the briquette in the relative positions as shown by Fig. 1. The interface between the two solids is, as Langmuir[4] has shown, the scene of the primary reaction, and it moves inward at a rate that is practically constant. Furnas,[5] Conley[6] and

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[3] Rivett, *The Phase Rule* (Oxford, at the Clarendon Press, 1923), p. 22.

[4] Langmuir, *J. Amer. Chem. Soc.*, 1916, **38**, 2263.

[5] Furnas, *Ind. Eng. Chem.*, 1931, **23**, 534.

[6] Conley, *Trans. Amer. Inst. Min. Met. Eng.*, 1942, **148**, 330.

Joseph [7] have found this to be the case in the calcination of calcium carbonate, which is also a case of simple decomposition.

Because the time for complete decomposition of CuS to Cu_2S was very short, less than 15 min at temperatures above 550° c., and because it was too difficult to stop the reaction after a specimen had been removed from the furnace, extensive rate measurements were not made on the primary reaction. The subsequent reactions were investigated by heating the CuS compresses in air at 550° c. until they were completely converted to Cu_2S, after which the pieces were transferred to a second furnace set at the desired temperature. The briquettes were withdrawn at varying intervals of time and boundary measurements made. The sliced cylinders looked like Fig. 2 and 3. Identification of the phases was accomplished by taking X-ray photograms of powdered samples from each zone, using characteristic cobalt *Kα* radiation in a Debye camera. The patterns of the unknowns were then compared with standards made of c.p. $CuSO_4$, Cu, Cu_2S, CuS, Cu_2O and CuO.

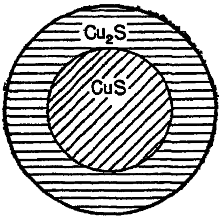

FIG. 1.—Partially roasted briquette of CuS.

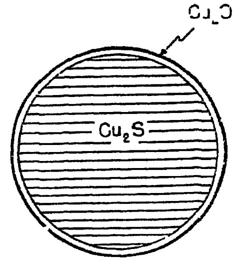

FIG. 2.—First stage in the roasting of Cu_2S.

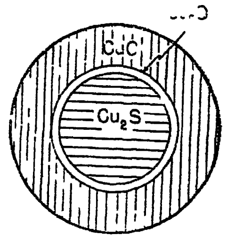

FIG. 3.—Second stage in the roasting of Cu_2S.

Results and Discussion

It could be concluded that under the conditions of the experiments at all temperatures from 430° to 965° c. the mechanism of the first stages in the roasting of cupric sulphide is represented by the following.

At the solid-solid interface,

$$2CuS(s) \rightleftharpoons Cu_2S\ (\beta) + \tfrac{1}{2}S_2(g) \quad . \quad . \quad . \quad (14)$$

$$S_2(g) \text{ at solid-solid interface, } \xrightarrow{\text{by diffusion}} S_2(g) \text{ at solid-gas interface} \quad . \quad (15)$$

and at the solid-gas interface,

$$\tfrac{1}{2}S_2(g) + O_2(g) = SO_2(g) \quad . \quad . \quad . \quad (2)$$

It is obvious that at the lower temperatures, where the rate of evolution and pressure of sulphur gas are low, reaction (2) may take place partly or wholly within the outer layer, and reaction (4) may also proceed.

TABLE I

THE RATE OF ADVANCE OF THE OXIDE LAYER IN THE ROASTING OF Cu_2S

Temperature ° c.	*Rate, in mm./min.*
430	0·0375
478	0·0385
525	0·0420
572	0·0480
663	0·0625
708	0·0690
787	0·080
873	0·0975
965	0·1065

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[7] Joseph, *Met. Tech.*, T. P. 1522, Dec., 1942.

For simplicity, we have considered in eqn. (14) that the sulphur gas is S_2. However, as shown by Kelley [8] in a critical survey, the gas resulting from (14) contains considerable quantities of S_8 and S_6. An extrapolation of semi-log plot of the work of Allen and Lombard,[9] giving the *total* sulphur pressure as a function of temperature, gives 495° C. as the temperature for which one atmosphere is the equilibrium sulphur pressure. As has been stated, the rate of sulphur evolution is relatively great, and, therefore, it seems unlikely that reactions (2) and (4) took place within the pores of the solid outer layer at temperatures greater than 495° C. Below this point the probability that these two reactions do occur in the aforementioned fashion increases inversely as some function of the temperature.

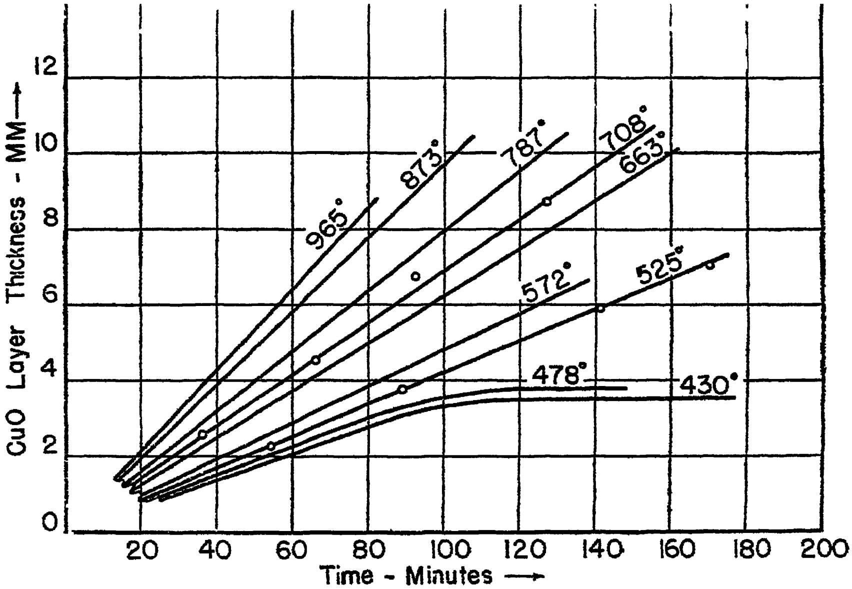

FIG. 4.—The thickness of the oxidised layer as a function of time at various temperatures.

The data for the second roasting stage, the oxidation of the Cu_2S, are summarised in Table I and Fig. 4 and 5. The rate of advance of the oxide layer was constant. In order not to confuse the drawing and to give a good idea of the conformity to lineality of the rate of advance of the phase boundary, experimental points have been inserted in Fig. 4 for only two of the temperatures—the best-fitting and the poorest.

Visual and X-ray examinations for all temperatures studied showed the solid phase in contact with the Cu_2S to be Cu_2O, as sketched in Fig. 2 and 3. The thickness of the cuprous oxide layer remained constant at a given temperature but varied with the temperature. At the lower temperatures it was about $\frac{1}{4}$ mm. thick, and $\frac{3}{4}$–1 mm. at the higher temperatures. Fig. 6 shows prints made from the Debye patterns of this phase and that of C. P. cuprous oxide. This means, then, that the cuprous oxide is the first product resulting from the roasting of Cu_2S. This does not agree with Ashcroft,[10] who in a paper describing the roasting of copper ores states: " The theory formulated and afterward found to be correct is as follows: Reaction in roasting proceeds primarily and definitely to the formation of sulphates and not of oxides, the latter being a secondary formation, and SO_2 is likewise a secondary product, that is to say, a product of decomposition of the previously formed sulphates."

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[8] Kelley, *loc. cit.*, pp. 5–11 and 38.

[9] Allen and Lombard, *Amer. J. Sci.*, 1917, **43**, 175. Corrections to this article are given in *Econ. Geol.*, 1937, **32**, 253.

[10] Ashcroft, *Trans. Electrochem. Soc.*, 1933, **63**, 23.

At temperatures above 663° c., CuO was the next and only solid phase to appear. Below 663° c., increasing amounts of sulphate were found intimately mixed with the cupric oxide. When the outer layer was wholly CuO, it was black, porous and easy to cut with a knife. The specimens containing sulphate became harder and less porous as the sulphate content increased until at 478° and 430° c. the pieces became so hard and dense as the time at temperature was made greater that the reaction practically ceased, as can be seen in Fig. 4.

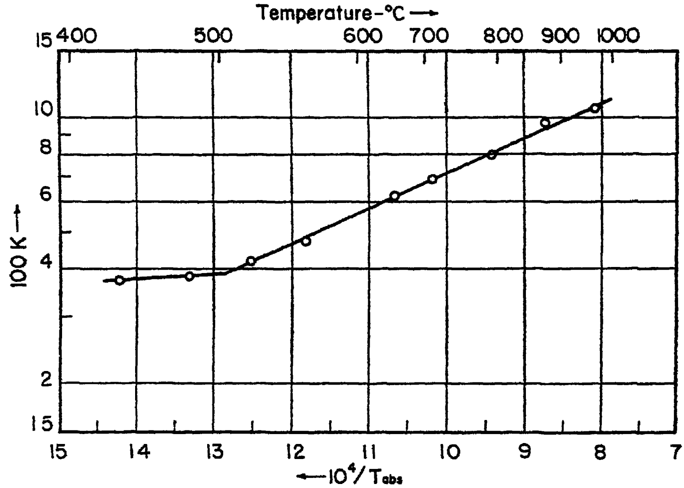

FIG. 5—Log of the rate of advance of the oxidised layer as a function of the reciprocal absolute temperature.

From the data plotted in Fig. 5 an apparent activation energy of 4·19 kcal./mol. is obtained for temperatures above 525° c. It is possible that the mechanism here is the relatively slow process of the diffusion of the reacting gas to the scene of the reaction through a film of counter-diffusing reaction products. The temperature coefficient of the diffusion rate of a gas may be given approximately by the expression:

$$D_2 = D_1 (T_2/T_1)^n \quad . \quad . \quad . \quad . \quad (16)$$

where D is the diffusion coefficient, T is the absolute temperature, and the constant, n, varies from 1·5 for an ideal gas to about 2·0 for actual gases at high temperatures. Calculation of relative diffusion rates from eqn. (16) for temperatures between 525° and 950° c. yield for the activation energy a value of about 3·9 kcal./mol.

The roasting of Cu_2S as carried out in our experiments can then be represented as follows.

For temperatures greater than 663° c.,

$$O_2(g) \text{ in the atmosphere} \xrightarrow{\text{by diffusion}} O_2(g) \text{ at the } Cu_2O\text{–}Cu_2S \text{ interface} \quad . \quad (17)$$

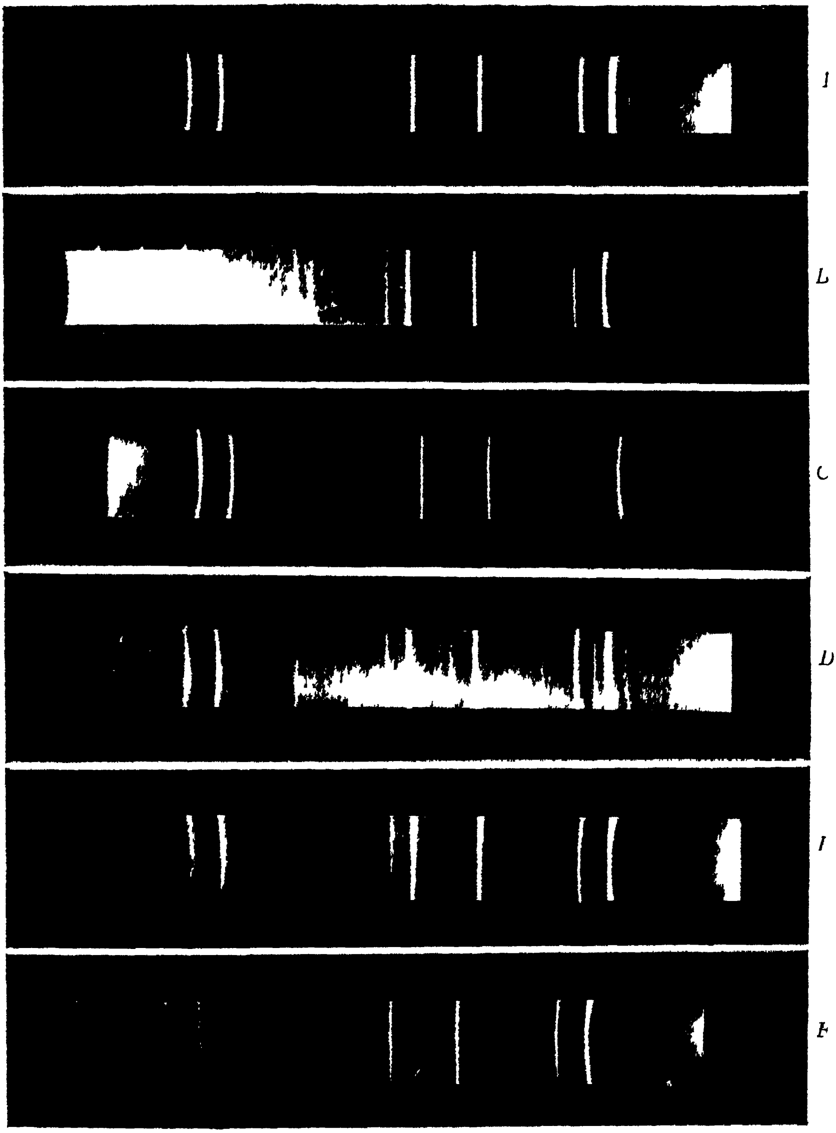

FIG 6.—X-ray photograms of c p Cu_2O and primary solid phase formed during the roasting of Cu_2S at various temperatures *A*—c p Cu_2O, *B*—965° c, *C*—787° c, *D*—663° c, *E*—572° c *F*—525° c.

At the Cu_2O–Cu_2S interface,

$$Cu_2S(\beta) + 1\tfrac{1}{2}O_2(g) = Cu_2O(s) + SO_2(g) \quad . \quad . \quad (18)$$

$$SO_2(g) \xrightarrow{\text{by diffusion}} SO_2(g) \text{ in the atmosphere} \quad . \quad . \quad (19)$$

At the Cu_2O–CuO interface,

$$Cu_2O(s) + \tfrac{1}{2}O_2(g) \rightleftharpoons CuO(s) \quad . \quad . \quad . \quad (20)$$

for temperatures below 663° c., (17), (18), (19) and (20) take place plus sulphatising reactions such as (4) and (5) occurring throughout the CuO layer.

The author is greatly indebted to Sam C. Carapella, Jr., Teaching Fellow in Metallurgy, University of Notre Dame, for helpful discussions and for aid in preparing the illustrations.

Summary

A new method for studying roasting reactions has been described. It has been shown by using the new procedure that the roasting of copper sulphides does not proceed primarily to the formation of sulphates, as has been previously reported, but rather to Cu_2S and Cu_2O in the case of CuS and Cu_2S respectively.

The mechanism of CuS roasting can be represented by the following sequence of reactions :

$$2CuS(s) \rightleftharpoons Cu_2S(\beta) + \tfrac{1}{2}S_2(g)$$
$$S_2(g) + \tfrac{1}{2}O_2(g) = SO_2(g)$$
$$Cu_2S(\beta) + 1\tfrac{1}{2}O_2(g) = Cu_2O(s) + SO_2(g)$$
$$Cu_2O(s) + \tfrac{1}{2}O_2(g) = CuO(s)$$

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AN ANALYSIS OF THE CONVERTING OF COPPER MATTE

BY E. A. PERETTI *

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In comparison with the length of time that man has known how to smelt copper ores, the converting of copper matte as it is practised at present is a relatively new process, having been in use for less than 70 years. The first successful application of the Bessemer converter in the copper industry is generally credited to Pierre Manhès whose invention in 1880 at Eguilles, France, consisted mainly in placing the tuyères at the sides of the vessel instead of at the bottom.[1] [2] Since Manhès' time great improvements have been made in design and operation—the engineering aspects of the process—but, unfortunately, the same can not be said of our knowledge of the chemistry involved, if one is to judge by the technical journals and text-books. This is particularly apparent to those of us engaged in teaching this unit process to the metallurgists of the future. It is the object of this paper to analyse certain phases of converting from the viewpoint of the instructor.

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[1] Peters, *Principles of Copper Smelting*, (McGraw-Hill Book Company, Inc., 1907), p. 452.

[2] Kelly and Laist, *Trans. Amer. Inst. Min. Met. Eng.*, 1933, **106**, 122.

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The Slag-forming Stage

While the shape and size of the converter vessel may affect the reactions taking place in it, this discussion will be confined to the Peirce-Smith or horizontal converter as it seems to be preferred to the vertical types, not only in newly constructed smelters,[3] but also in the older ones that have been using the upright type ever since its invention.[4] To simplify the discussion, the liquid matte will be considered as consisting solely of copper, iron and sulphur, and the flux will be regarded as silica.

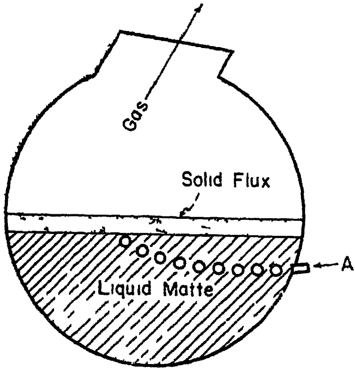

FIG. 1.—The copper converter at the start of the slag-forming stage

At the start of the blowing, the physical conditions in the converter are as sketched schematically in Fig. 1—a layer of liquid, through which air is being blown, and upon which is floating the solid flux; the temperature is between 1100° and 1300° C. The main reaction occurring is usually represented as follows:

$$FeS(l) + 1\tfrac{1}{2}O_2(g) = FeO(l) + SO_2(g) \quad . \quad (1)$$

The iron oxide eventually reacts with the silica flux to form a liquid slag layer above the matte.

A thermodynamic calculation for eqn. (1) yields the following for the heat content and free-energy changes as a function of temperature, using the nomenclature of Lewis and Randall:[5]

$$\Delta H = -108{,}000 - 6{\cdot}705T + 2{\cdot}585 \times 10^{-3}T^2 \quad . \quad (2)$$

$$\Delta F^\circ = -108{,}000 + 15{\cdot}45T \log T - 2{\cdot}585 \times 10^{-3}T^2 - 27{\cdot}5T \quad . \quad (3)$$

from which we obtain at 1500° K., $\Delta F^\circ = -40{\cdot}75$ and $\Delta H = -112{\cdot}25$ kcal., and an equilibrium constant, K, of $8{\cdot}5 \times 10^5$.

$$\text{Since } K = \frac{a_{FeO} \cdot f_{SO_2}}{a_{FeS} \cdot f_{O_2}^{1{\cdot}5}} \quad . \quad . \quad . \quad . \quad (4)$$

it is evident that the SO_2/O_2 ratio could be very large before equilibrium would be attained. When blowing with air, the maximum SO_2 content of the exit gas according to eqn. (1) would not exceed 15 % by volume; hence, the oxygen utilisation theoretically could be almost 100 %. This figure is approached in actual practice.

The questions then arise: Does eqn. (1) represent the mechanism of the reaction or is it described by the following (to mention only one of several possibilities)?

$$FeS(l) + \tfrac{1}{2}O_2(g) = FeO(l) + \tfrac{1}{2}S_2(g) \quad . \quad . \quad . \quad (5)$$

$$\tfrac{1}{2}S_2(g) + O_2(g) = SO_2(g) \quad . \quad . \quad . \quad (6)$$

The standard free-energy changes for (5) and (6), computed at 1500° K. from data by Kelley,[6] are −24·1 and −60·7 kcal. respectively.

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[3] Buch, *Met. Tech. Amer. Inst. Min. Met Eng.*, T.P. 2248, Dec., 1947.
[4] Peretti, *Eng. Min. J.*, 1943, **144**, 101.
[5] Lewis and Randall, *Thermodynamics* (McGraw-Hill Book Company, Inc., 1923).
[6] Kelley, *U.S. Bur. Mines Bull.*, No. 406, 1937, pp. 13 and 126.

Furthermore, is the reaction mechanism one of oxygen dissolution in the matte followed by a homogeneous reaction in the liquid phase or is it completely heterogeneous with the gas-liquid interface as the only place where oxidation of the matte occurs ? Integral parts of these questions are similar ones regarding the oxide resulting from the reaction. Published accounts of the converting process infer that the oxide is formed as a separate phase which rises to the matte surface to combine with the silica. A glance at some of the very few matte density values available in the literature,[7] 4·8, 5·18, 5·42 and 5·5 g. cm.$^{-3}$ for 13·62, 43·0, 60·2 and 80·0 % copper contents, respectively, as compared to 5·7 g. cm.$^{-3}$ for FeO makes one wonder about the matter. (It is appreciated that these figures are for the solids at room temperature and more pertinent would be the values at converting temperatures.) It is possible that the iron oxide already present in the matte as it comes from the reverberatory furnace reacts with the silica at the solid-liquid interface, and that the oxide formed by the blowing counteracts this diminution of the oxide content of the sulphide liquid by dissolving in it, if a heterogeneous oxidation reaction prevails, or by being formed in it, if the reaction is homogeneous.

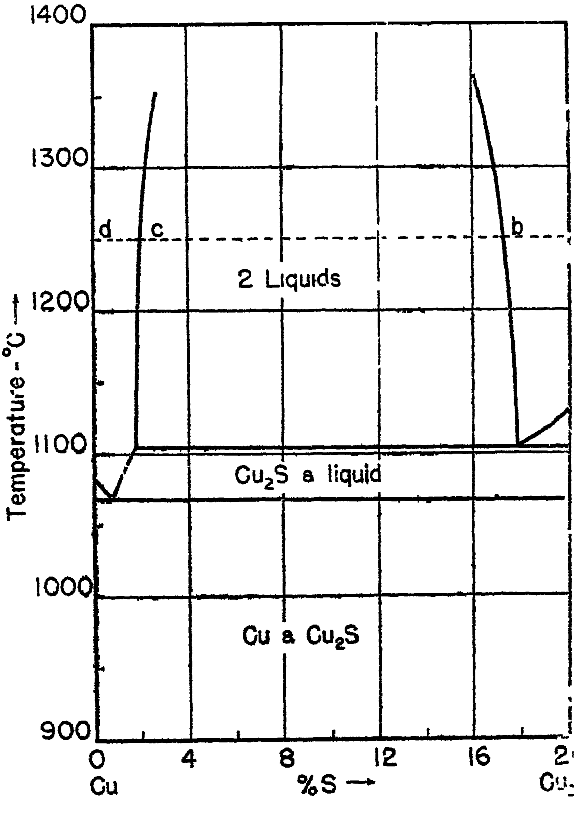

FIG. 2 —A portion of the copper-sulphur phase diagram.

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[7] Peters, *loc. cit.*, p. 413.

Turning our attention now to the copper in the matte during the slag-forming stage, we find that very little leaves the sulphide phase in the presence of iron. The equations most often given to represent this are:

$$Cu_2S(l) + 1\tfrac{1}{2}O_2(g) = Cu_2O(l) + SO_2(g) \quad . \quad . \quad (7)$$

$$Cu_2O(l) + FeS(l) \rightleftharpoons Cu_2S(l) + FeO(l) \quad . \quad . \quad (8)$$

The questions that were raised regarding eqn. (1) would also apply to (7). Here, too, the calculated equilibrium constant at 1500° K. is of sufficient magnitude, $3{\cdot}6 \times 10^9$, that a very large SO_2/O_2 ratio would be necessary for equilibrium. Kelley [8] has computed the standard free-energy change for (8) to be approximately equal to $-21{\cdot}870 - 2{\cdot}40T$, from which he deduced, with certain simplifying assumptions, that if equilibrium is established, only a small concentration of Cu_2O is built up in the slag until the FeS concentration becomes small. The copper content of slags produced in converter plants rarely exceeds 5 %, and it is estimated that only about 10 % of this is oxide.[9] [10] From these facts one must conclude that either (*a*) the copper is oxidised at an appreciable rate and is then returned to the matte by reaction with the iron or (*b*) the rate of copper oxidation in the presence of iron is very small. Either alternative could give the same end-result, but the mechanisms would necessarily be different.

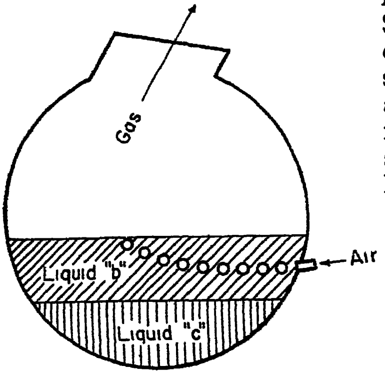

FIG. 3—The copper converter during part of the blister-forming stage.

The Blister-forming Stage

If, for simplicity, we consider the "white metal" to consist of only copper and sulphur and neglect the solubility of oxygen in this phase as blowing proceeds, it will enable us to use a portion of the copper-sulphur phase diagram,[11] Fig. 2, to depict the course of events in the converter during this stage of the process. At a temperature of 1250° C., for example, as blowing continues, the concentration of sulphur in the liquid is changing along the line *a d*, and only one liquid phase will be present in the vessel under equilibrium conditions until *b* is reached. At this point a second phase, a copper-rich liquid of composition *c*, appears and being heavier than the liquid *b*, it sinks to the bottom of the converter. These two liquids will remain in the converter (Fig. 3) until point *c* is attained. Furthermore, the composition of each phase remains the same, although the quantity of sulphur-rich phase is diminishing until it is zero at *c*, and the mass of the copper-rich phase is increasing until it is a maximum at *c*. Blowing beyond this point would be done again with only one liquid in the container until *d*, the theoretical end-point, is reached.

By applying the lever principle for phase diagrams, letting *t* equal the total time in minutes required for the theoretical blister-blowing stage, and making the assumption that the rates of blowing and sulphur elimination remain constant throughout, we arrive at the following conclusions.

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[8] Kelley, *loc. cit.*, p. 136.

[9] Newton and Wilson, *Metallurgy of Copper*, (John Wiley and Sons, Inc., 1942), p. 175.

[10] Wartman and Boyer, *U.S. Bur. Mines*, Reports of Investigations 2985, 1930.

[11] Hansen, *Der Aufbau der Zweistofflegierungen*, (J. Springer, Berlin, 1936), p. 611.

(1) The elapse of time between the starting of the blow and the appearance of the second liquid phase is 0·1373 t min.

(2) Two liquid phases are present in the converter for 0·7451 t min.

(3) Blowing is being carried out on material containing more than 2 % copper for 0·8824 t min.

(4) Copper-rich liquid would be blown for 0·1176 t min.

The stoichiometry of the blister stage is given by:

$$Cu_2S(l) + O_2(g) = 2Cu(l) + SO_2(g) \quad . \quad . \quad . \quad (9)$$

It is not known at present whether or not this equation represents the mechanism. Some authors seem to infer that the copper reduction takes place in two steps:

$$Cu_2S(l) + 1\tfrac{1}{2}O_2(g) = Cu_2O(l) + SO_2(g) \quad . \quad . \quad (7)$$

$$Cu_2S(l) + 2Cu_2O(l) = 6\ Cu(l) + SO_2(g) \quad . \quad . \quad (10)$$

Proof of this mechanism is lacking also, and other possibilities exist. Questions similar to those raised in connection with the first blowing stage could also be asked here. The answers to these queries, were they available, would make a great deal of difference in our thinking regarding the theory and, perhaps, even in the practice of converting.

Bottom-Blowing

The attempts made to apply the bottom-blown converter used in the steel industry to the treatment of copper mattes ended in failure. By examining Fig. 2 and 3, it can be seen that for approximately 14 % of the total blowing time, bottom-blowing, and side-blowing would be done on material of exactly the same composition. However, after point b is reached, the bottom-blown converter would have its tuyères in contact with the copper-rich liquid, and sulphur would have to be transferred to this phase from the superimposed liquid, largely by diffusion. This would be accomplished at diminishing rates as the volume of the copper-rich phase increases and would probably be followed by the formation of increasing amounts of Cu_2O:

$$2Cu(l) + \tfrac{1}{2}O_2(g) = Cu_2O(l) \quad . \quad . \quad . \quad (11)$$

By combining some of Kelley's[12] calculations there is obtained:

For eqn. (9)

$$\Delta H = -53{,}105 - 5{\cdot}87T + 0{\cdot}576 \times 10^{-3}T^2 + 0{\cdot}165 \times 10^5T^{-1} \quad (12)$$

and at 1500° K., ΔH is $-60{\cdot}62$ kcal.;

For eqn. (11)

$$\Delta H = -36{,}590 + 4{\cdot}86T - 0{\cdot}06 \times 10^{-3}T^2 - 0{\cdot}938 \times 10^5T^{-1} \quad (13)$$

and at 1500° K., ΔH is $-29{\cdot}5$ kcal.

If the rates of oxygen consumption in reactions (9) and (11) were equal, the rates of heat generation would be approximately the same also ($-60{\cdot}62$ compared to $2 \times -29{\cdot}5$, or -59 kcal). Apparently, this is not the case, and because of the slow replenishment of the sulphur in the lower layer the rate of heat liberation is too small to keep the contents of the converter liquid; as a result the tuyères become plugged with solids, and the process stops.

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[12] Kelley, *loc. cit.*, p. 129.

Summary

A critical survey of converting reactions has been presented from the viewpoint of the teacher of extractive metallurgy. Stress is placed on the fact that actually very little of the physical chemistry of the operation appears to be known. Drawings that help to understand some of the physical conditions in the converter during the two blowing periods are included.

An attempt is made to clarify, particularly for the student, the reasons for the failure of bottom-blowing.

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THE REDUCTION OF OXIDES OF IRON AS A DIFFUSION—CONTROLLED REACTION

By S. E. Woods

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1. Introduction

Gaseous reduction of the oxides of iron is carried out on a scale far exceeding that of any other metallurgical process. Not unnaturally therefore these reductions have received considerable attention experimentally, in the first place from the point of view of the equilibria involved and more recently in connection with the rate of reaction under different conditions. A number of investigators have expressed the view that the rate of reduction, under certain conditions at least, is limited by the rate of access of the reducing gas to the surface of unreduced iron oxide. However, the consequences of this limitation of reaction rate by a diffusion process have been at best imperfectly realised and in some cases incorrectly stated.

Certain types of evidence pointing to diffusion control (e.g., small temperature coefficient, relation between rates with hydrogen and with carbon monoxide) do not require for their interpretation any precise understanding of the mass transfer system involved. In general, however, this is not the case. In dealing with such matters as the influence of particle size or of gas velocity, or with the variation of the reaction velocity with completeness of reduction of a given specimen, one finds, at least if diffusion control is assumed, that the behaviour is a function not only of the system iron oxide —reducing gas, but also of the details of the experimental system used.

It seems worth while therefore to examine the different types of experimental method which have been used in investigating the gaseous reduction of iron ores, starting in each case with the assumption of a reaction rate controlled by gas diffusion to and from the reacting surface, in order to determine what sort of behaviour can be expected in each case. This examination should not only provide a critique of these experimental methods, but by comparison with observation should also show how much of the experimental behaviour can be understood in terms of a reduction rate limited by diffusion, and on the other hand what are the anomalies remaining for explanation on which experimental attention should be concentrated.

The following aims to provide in brief outline such a critical examination. No attempt is made to deal with all the numerous published investigations of gaseous reduction of iron ores; attention is confined to a small number of papers which seem most instructive from the point of view of the Discussion.

The reduction of hæmatitic ore is first considered, dealing in turn with reduction of a bed of the material by a gas flowing through it, with reduction of individual shaped cubes of the ore, and with reduction of the sample contained in a boat. The special features of the reduction of magnetite are then discussed.

2. Reduction of a Bed of Ore

The main features of the flow system in this case are represented in the reaction model shown in Fig. 1. The ore is considered to form the walls of a tube through which the gas flows. Diffusion from the exterior surface of the particles into the flowing gas-stream will have a characteristic average rate dependent upon gas velocity; this is symbolised formally in terms of a core of completely mixed gas moving at uniform velocity, with a hypothetical still layer of thickness d related to gas velocity. The equivalent thickness of the layer of oxide on the wall of the tube is related to the size of the particles composing the bed; the more uniform is the size of the gas channels through the bed, the closer will the thickness of the oxide layer correspond to reduction of a single particle.

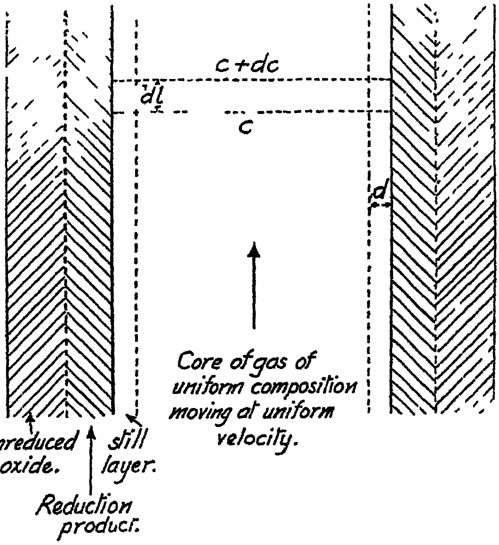
c+dc
dl
c
d
Core of gas of uniform composition moving at uniform velocity.
Unreduced oxide.
still layer.
Reduction product.

FIG. 1.—Reaction model for flow through bed of broken solid.

To simplify matters, consider a single stage of reduction, say, FeO → Fe. When this stage is still incomplete there will be a layer of porous iron and a more-or-less sharp interface separating this from unreduced oxide. At the interface (the sharpness of which depends upon the detailed kinetics of the reduction, but is not critical for the diffusion calculation) the gas composition is by hypothesis that corresponding to the equilibrium:

$$FeO + CO \rightleftharpoons Fe + CO_2,$$

while in the well-mixed core the gas composition is determined by the "reaction history" of the gas in the preceding section of the tube. Between these limits of composition, diffusion takes place through the successive layers (a) of gas, of thickness d, (b) of porous reduction product. Diffusion through the layer of porous solid may take place either through the gas-filled pores, or through the crystal lattice itself; the latter will be very much the slower process and, with the porous reduction products one is dealing with, it appears that it is diffusion through the gas-filled pores which is important.

The mathematical estimate of the course of the reduction, as a function of elapsed time and of distance along the tube, is greatly simplified if either of the film resistances, that of the gas film or that of the layer of porous solid, can be neglected in comparison with the other. It appears that under typical laboratory conditions the reduction of a porous hæmatite ore corresponds to the case in which the resistance to diffusion of the layer of porous reaction product is negligible. This statement is based upon the observations of Marek, Bogrow and King.[1] These authors show that the results of a large number of experiments, in which a bed of ore of constant geometry was reduced by a stream of synthetic blast-furnace gas of constant composition, with velocities varied over a tenfold range and with absolute pressures varied over a fivefold range, could be brought into concordance in the following way.

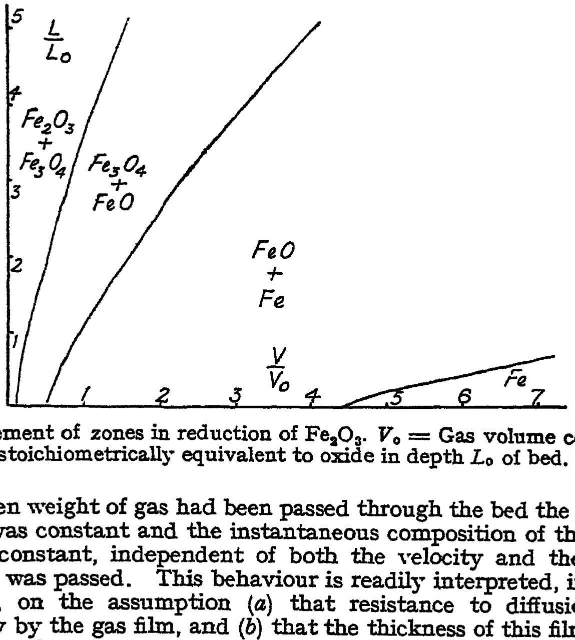

FIG. 2.—Movement of zones in reduction of Fe_2O_3. V_0 = Gas volume containing CO stoichiometrically equivalent to oxide in depth L_0 of bed.

When a given weight of gas had been passed through the bed the total amount of reduction was constant and the instantaneous composition of the gas leaving the bed was constant, independent of both the velocity and the pressure at which the gas was passed. This behaviour is readily interpreted, in the present writer's view, on the assumption (*a*) that resistance to diffusion is offered predominantly by the gas film, and (*b*) that the thickness of this film is inversely proportional to the first power of the mass velocity. The second assumption is reasonably in line with the behaviour in heat-transfer and mass-transfer systems, from which one might have expected d to be proportional to (mass velocity)$^{-0.85}$; and the special characteristics of a system of gas channels of very diverse sizes give one good grounds for assuming an exponent even closer to -1. If, however, one assigns any appreciable film resistance to the layer of porous reaction product it becomes impossible to account for Marek's generalisation.

The course of the reduction over the successive stages, $Fe_2O_3 - Fe_3O_4$, $Fe_3O_4 - FeO$, $FeO - Fe$, can be calculated on this simplified reaction model, as follows.

The CO_2 concentration C in the gas increases with distance along the tube according to the equation:

$$V\frac{dC}{dl} = DS \cdot \frac{C_e - C}{d}$$

where V = volume of gas/unit time, D = diffusion coefficient of CO_2 in gas, S = surface area of tube wall per unit length of tube, and C_e = equilibrium CO_2 concentration for appropriate reduction stage.

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[1] Marek, Bogrow and King, *Met. Tech.*, T.P. 2184, June 1947.

This gives

$$\frac{C_e - C}{C_e - C_0} = e^{-\frac{(L-L_0)}{L_0}}$$

where $L_0 = Vd/DS$ is a characteristic length which we have assumed to be independent of velocity (since $d \propto V^{-1}$).

Suppose that reducing gas were passed through an infinite bed of material initially present as Fe_2O_3; this bed is characterised by a length parameter L_0. A simple analysis shows that until a quantity of gas has been passed which, equilibrated with Fe_2O_3 and Fe_3O_4, would reduce the Fe_2O_3 contained in a length L_0 of this bed to Fe_3O_4, then there will be at all points a mixture of Fe_2O_3 and Fe_3O_4. At this stage the element of the bed over which the gas first passes becomes denuded of Fe_2O_3; the Fe_2O_3-interface then travels forward at the calculated stoichiometric rate. In the region denuded of Fe_2O_3 the similar process of reduction of Fe_3O_4 to FeO then takes place with, of course, the new appropriate value of C_e. An illustration of the manner in which the successive interfaces move in the direction of gas flow is given in Fig 2; the calculations were made for the "rich mixture" conditions of Marek *et al.* The ordinate is distance along the bed measured in units of L_0, the abscissa quantity of gas passed in units of V_0, the volume of gas containing CO stoichiometrically equivalent to complete reduction of the Fe_2O_3 in a depth of bed L_0.

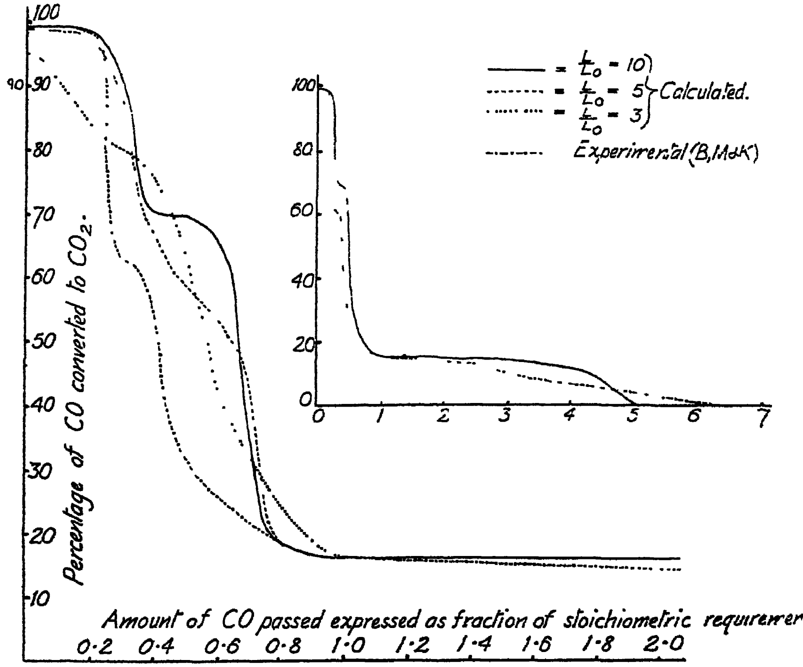

FIG. 3.

With a bed of finite depth, the calculation of the instantaneous CO_2- content of the gas leaving the bed after passage of a given volume of gas follows fairly obviously. Curves calculated in this way for the conditions of Fig. 2 are given in Fig. 3, where the abscissa is now measured in stoichiometric equivalents of the whole bed. Marek's experimental curve is also shown, displaced, as these authors suggest is necessary, by 0·1 unit along the abscissa. Actual bed conditions correspond to flow in parallel through a number of channels, some of which will reach a given stage of reduction more quickly, in elapsed time if not in volume passed, than others. The experimental curve is in reasonable agreement with this conception.

It will be clear that under these conditions this experimental method is uninformative as to processes within the individual ore particles, and rather insensitive even to changes in the packing characteristics of the bed. One might improve this latter sensitivity by using a thinner bed, but there would then probably be difficulties in obtaining a reproducible packing. If for any reason the ore is less "reducible," the method becomes more revealing as to processes within the individual particle, until with dense magnetite ores, as will be seen later, the resistance of the gas-film becomes of negligible importance and the rate of reduction of the bed reflects closely the behaviour of individual particles bathed in the reducing gas. However, over a wide range of reducibility, which is of interest in practice, experimental reductions of beds of ore are a very insensitive index of processes within the individual particle.

To provide a correct picture of the behaviour in the stock column of a blast furnace, it would be necessary in experimental reductions of beds of ore to employ much higher rates of flow than have been customary. The size of ore particle used in this type of experiment will be not greater than one tenth that used in industrial practice. To obtain a similar relative importance of gas-film and porous solid resistances it would then be necessary to work with a linear gas velocity at least ten times that of industrial practice. This would mean an experimental gas velocity of about 10 cubic feet N.T.P./sq. in. (With such a tenth-scale system, the time required to reach any given stage of reduction would be $1/10^2$ of that required on full scale.) Even with conditions correctly chosen for dynamical similarity, errors might arise however for the following reason; in the bed of ore there are two essentially unrelated pore systems, one of interparticle voids with characteristic dimension proportional to the particle size, and one arising from the porosity of the particles themselves and of the reduction products. The scale of this second pore system remains unaltered in laboratory experiment, so that under laboratory conditions flow of gases through the particles themselves is exaggerated in comparison with its incidence in large-scale practice.

3. Reduction of Cubes of Ore

A method which has been used by a number of investigators consists in reducing cubes cut from the ore, in a stream of hydrogen, in a conventional tube furnace. The following treatment provides a starting point for discussion of this method. For obvious reasons of simplicity we consider reduction of a sphere of radius r_0. The flow of gas around the sphere establishes a certain overall transfer coefficient from the surface of the sphere to the body of the gas; this coefficient is not uniform over all elements of the surface but as an approximation will be regarded as being so, so that we use a parameter f for the thickness of a hypothetical still layer of gas surrounding the particle.

If the diffusion coefficient of water vapour in the ambient gas is D, that of water vapour through the porous layer of reduction products is written βD, where β, of course, is less than unity. For a single stage of reduction we then obtain the time to reach a fractional reduction $(1 - \alpha^3)$. (αr_0 = radius of sphere of unreduced oxide)

$$\frac{t r_0}{M} = \frac{3.}{4\pi D(C_e - C_0)} \left[\frac{\frac{1-\alpha^2}{2} - \frac{1-\alpha^3}{3}}{\beta} + \frac{f}{r_0 + f} \; \frac{(1-\alpha^3)}{3.} \right]$$

where M = total amount of H_2O formed by complete reduction of sphere,
C_e = equilibrium concentration of H_2O, and
C_0 = ambient concentration of H_2O.

The quantities typical of the ore, which enter into this expression, are M, representing essentially the reducible oxygen per unit volume of the ore and β which is a measure of the ease of diffusion through the porous reduction products. The other factors determining rate of reduction are properties either of the gas or of the experimental set-up

Reduction of a sphere composed initially of either Fe_2O_3 or Fe_3O_4 will proceed by stages; we can in the first place neglect this aspect of the reduction which is not of critical importance if the reaction is in fact diffusion controlled.

The factor β will be expected to be a function of the porosity of the sponge iron formed by reduction. Diffusion through the gas-filled pore system should depend upon the fractional volume of the pores and upon the geometry of these pores but not upon the scale (mean diameter) of the pore system; in this respect it is unlike permeability which is extremely dependent upon pore diameter. Diffusion will, however, be sensitive to the size of pores which are not large in comparison with the mean free path of the gas molecules. If the pore system consisted of parallel capillaries with axes normal to the surface, the factor β would equal the fractional porosity. Owing to the complicated nature of the pores we should expect β to have a smaller value than this and to depend upon a higher power of the porosity.

We can examine from this point of view the results of Joseph[2] who studied the reduction in hydrogen at 800° c. of 9/16" cubes of a wide range of ores. He showed that porosity of the ore was the principal factor determining time to 90 % reduction but did not distinguish between the two aspects of porosity in this connection (*a*) its effect upon oxygen content per unit volume and (*b*) its bearing upon diffusion through the layer of reduction products.

A tabulation of the quantity

$$\frac{tl}{M} = \frac{(\text{time to } 90\ \%\ \text{reduction}) \times (\text{cube edge})}{[\text{total weight of water formed}]}$$

for the very large number of determinations made by Joseph, shows that $\frac{tl}{M}$ is much more constant than the time itself but that there remains a variation with porosity and with ore composition, the higher values of $\frac{tl}{M}$ being associated with low porosity and with low iron content. We shall not deal further with the question of ore composition. As regards porosity, Fig. 4 gives a plot of $\frac{tl}{M}$ against apparent density for a selected group of data from Joseph's paper (ores other than limonites for which total H_2O formed exceeds 0·3 ore weight). Apparent density is used as independent variable rather than the calculated porosity because of better correlation; presumably the measured variations in "true density" within this group of samples were illusory. Although there are some large individual deviations the general behaviour is clear; the value of $\frac{tl}{M}$ is approximately doubled in passing from very porous to very dense ores.

Inserting the absolute value of D in the equation given above enables one to estimate the value of β. In order to eliminate f, the difference in $\frac{tl}{M}$ for dense and porous ores is used in the calculation. A diffusion coefficient for H_2O in H_2 at 800° c. of 8·2 cm.^{2}/sec. leads to the equation

$$\left(\frac{1}{\beta}\right)_{\text{apparent density } 4\cdot5} - \left(\frac{1}{\beta}\right)_{\text{apparent density } 3\cdot0} = 8.$$

Further considerations suggest that for the most porous ores β is about 0·1 and for the least porous about 0·05. These values are not unreasonable, bearing in mind that we are concerned mainly with a layer of sponge iron with a minimum porosity of over 50 %.

Lewis[3] presents data for cubes of different sizes cut from two ores. It is difficult, however, to extract from his experimental data any precise information as to the true effect of cube size since :

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[2] Joseph, *Trans. Amer. Inst. Min. Met. Eng.*, 1936, **120**, 72.

[3] Lewis, *Met. Tech.*, T.P. 2177, June, 1947.

(*a*) with the larger cubes the H_2O concentration in the issuing gas attains values exceeding 50 % of the equilibrium value : under these conditions it is difficult to assign a value for the mean effective concentration of H_2O in the ambient gas ;

(*b*) when one looks at all closely into the nature of the gas flow around cubes of varying size resting on the wall of a cylindrical tube, it is clear that the effective film thickness f will vary in a complicated manner.

With these provisos, however, the results correspond to reasonable constancy of $\frac{tl}{M}$; this corresponds to a time of reduction proportional to (cube dimension)^2.

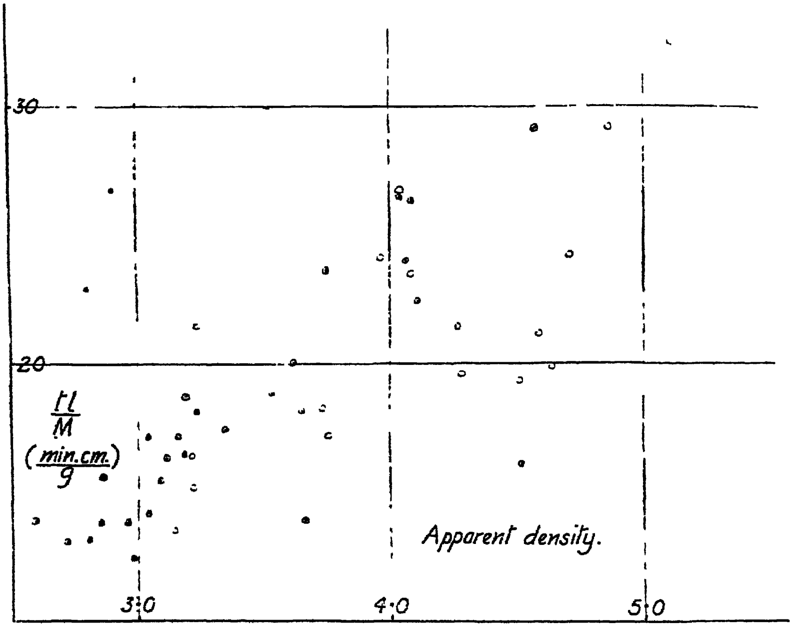

FIG. 4.—Data of Joseph (*Trans. Amer. Inst. Min. Met. Eng.*, 1936, **120**, 72). Selected data $\frac{\text{Total } H_2O}{\text{Ore Wt}} > 0{\cdot}3$

Similar difficulties arise with regard to the comparison of times of reduction to 50 %, 80 %, 90 %, completion. Owing to rather large presumed values of f, and to inadequate supply of reducing gas, the rate of reduction falls off much less sharply as reduction proceeds than would be the case under conditions of practical interest.

One can conclude, therefore, that the method of reduction of cubes of ore does provide valid information as to the reduction characteristics of the ore ; it would be considerably more informative if the influence of the external flow conditions were exactly calculable or, better, were negligible in comparison with diffusion within the particle.

An aggregate of crushed ore contained in a boat is a quasi-porous body cut to the shape of the boat with gas access restricted to one face. Since the porosity is only partly that of the ore itself this method will be less instructive than that using shaped pieces of ore, and is no more calculable as regards gas flow conditions.

4. Reduction of Magnetite

The reduction of dense magnetite presents a number of differences from the reductions considered above. The work of Udy and Lorig [4] may be quoted to illustrate the main points.

(1) The rate under corresponding conditions is very much slower. One can compare Udy and Lorig's reductions of beds of ore with the experiments of Marek, Bogrow and King already discussed, and the same authors' reductions of single particles with Joseph's work. In reducing a bed of crushed magnetite one arrives, at quite moderate gas velocities, at a condition such that variation of gas velocity has no further appreciable influence on rate ; this corresponds to processes within the individual particle (whether of diffusion or of intermolecular rearrangement) dictating the overall rate. The time required to reduce a particle of magnetite 1/10″ diam. is similar to that required for the reduction of a 9/16″ cube of a dense hæmatite.

(2) At temperatures of about 600° c. and higher, the reaction rate diminishes with exceptional rapidity as reduction proceeds, so that although the initial rate increases with temperature the mean rate to, for example, 90 % completion falls with increasing temperature in the region 600°–700° c. The extent to which this effect is observed depends upon the experimental method adopted.

(3) The results of experiments carried out by Udy and Lorig with beds of different depths reveal, as the authors conclude, a non-linear dependence of rate upon "distance from equilibrium" in gas composition; increasing H_2O concentration in the later layers of the bed traversed by the gas resulted in a very large diminution in reduction rate. The interpretation of this effect offered by the authors seems untenable.

Clearly, if the more rapid reduction processes already discussed are in fact limited in rate by gas diffusion, then the surface at which reduction occurs must be in contact with gas approximating more or less closely to equilibrium composition. Under these conditions, Fe_3O_4 must be an intermediate stage in reduction of Fe_2O_3. The faster rates of reduction with hæmatite ores can only be attributed therefore to a considerably greater accessible surface area per unit volume of the magnetite produced as an intermediate in the reduction of Fe_2O_3, compared with a dense magnetite ore. Presumably the same molecular processes take place in the reduction of this intermediate as in reducing the magnetite ore, but are concealed from experimental observation in measurements of rate by overriding considerations of diffusion through gas-films or through gas-filled pores.

Below 565° c., reduction of Fe_3O_4 can proceed only to formation of metallic iron. This process, associated with a large diminution of volume, and with no intermediate solid solutions, can be expected to yield an outer layer of iron of small crystal size and well-distributed porosity.

Above 565° c., FeO may exist as an intermediate stage. This introduces a number of possibilities of slow processes hindering reduction. There may be an intrinsically slow rate of reduction at an FeO — Fe interface ; alternatively, the reduction proceeding via a continuous series of solid solutions might mean that a crystal of FeO was surrounded by a reduced layer of varying composition through which either oxygen or hydrogen and water vapour must diffuse by a slow solid diffusion process.

FeO is, however, not necessarily formed. Since the rate of reduction of magnetite is considerably slower than the limiting diffusion rate the gas in contact with the Fe_3O_4 surface will approximate in composition to the main stream of reducing gas, which may be such that it is in equilibrium with metallic iron. The intermediate reduction stage might then be omitted either because of a reduction directly to metallic iron or because the FeO formed was capable of only transient existence. The extent to which FeO was an intermediate might then depend rather sensitively upon the composition of the ambient gas. The situation would have some analogies with the behaviour in removal of water from hydrates, where an intermediate hydrate exists. The effect of H_2O

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[4] Udy and Lorig, *Trans. Amer. Inst. Min. Met. Eng.*, 1943, **154**, 162.

concentration in H_2 reduction of magnetite referred to above may possibly arise in this way.

Despite the possible intervention of these slow processes, the intrinsic rates involved in the reduction of a hæmatite, proceeding as we believe via all possible intermediate stages, are rapid enough for the process to be limited by rates of diffusion through gas-films. This can only mean that such questions as the size and distribution of gas pores, the area per unit volume of surface accessible to gas, the maximum distance from any point in the solid to a surface accessible to gas, are of decisive importance in relation to reaction rate; it is, of course, not only with the original ore but also with its several stages of reduction that we are concerned.

5. Discussion

The foregoing treatments are oversimplified in many respects, but serve to show that analysis in terms of a rate controlled by diffusion through gas either adjacent to the surface or filling the pores of the solid, is a correct starting-point, except possibly for the reduction of dense magnetite. The more detailed one's examination of a given case the less satisfactory will this simple treatment be; the defects may well be, however, not in the assumption of gas diffusion control, but in the fact that the pore systems encountered in practice are more complex than has been allowed for.

Suppose that one were to imitate the pore system of a porous solid by fitting together an aggregate of non-porous particles. The particles might be systematically packed with a consistent average fractional volume of voids; this would correspond to a uniform pore system, and clearly in an aggregate made up in this way the resistance offered to diffusion between any two points separated by a large number of particle diameters would be proportional to the distance between the points. The effective diffusion coefficient would be some function of the average porosity. Alternatively, however, the particles might be packed in the first place into low-voidage aggregates which were then assembled in a relatively loose packing. In this case the resistance offered to diffusion between two points would depend not only on the distance between the points but also on the distance separating each point from the boundary of its own particular tightly packed aggregate. This example shows that in certain circumstances the distribution of pore volume as well as its total volume can be a determining factor in a diffusion-controlled process.

The unreduced ore might have a pore structure of some complex type such as was indicated above; this is even more to be expected however of the partly reduced ore, in which crystals of the higher oxide have been transformed into aggregates of crystals of reduction products of considerably smaller volume. In order to understand the alterations in the pore system as reduction proceeds it would be necessary to evaluate the factors which dictate the size of the crystals of the reduction products and the location of the pore volume necessarily arising when these products are formed. The process would be expected to be different for reduction of Fe_3O_4 directly to the metallic state from its reduction via an FeO stage. In the latter case, if a film of iron of low, but appreciable, porosity were formed around the unreduced oxide, this would provide a duplex pore system similar to that referred to in the last paragraph and very slow reaction rates might still be controlled by gas diffusion in pores; for sufficiently low values of the porosity of the film, processes of diffusion in the crystal lattice would become rate-controlling.

The formation of solid solutions with corresponding ranges of continuously variable equilibrium CO_2/CO ratio, is another complicating factor. It is clear, therefore, that very complex behaviour can arise despite the fact that the rate-controlling process is the essentially simple one of gaseous diffusion. The diffusion mechanism does not necessarily lead to simple mathematical solutions. It is, however, particularly helpful in the following respects—

(*a*) It provides answers of at least approximate validity to a number of questions which are of practical importance in smelting operations.

(*b*) It directs attention to one particular aspect of the problem of ore reduction, i.e., the nature of the pore systems encountered in practice at all stages of reduction and the factors governing the development of pores during reduction.

(*c*) In relation to the design of experiments it enables one to avoid conditions, which are all too easy to obtain, under which the observations measure characteristics of the apparatus rather than of the system in which one is really interested

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A KINETIC STUDY OF THE DISSOCIATION OF CARBON MONOXIDE ACCOMPANYING THE REDUCTION OF METALLIC OXIDES

BY A. JULIARD, R. RAYET AND A. LUDÉ

Received in French, 16th June, 1948 ;
translated by J. H. E. Jeffes

This work provides a contribution to the controversial question of the catalytic action exerted by various solid phases on the Boudouard reaction during the reduction of metallic oxides by carbon monoxide. Greater precision of measurement of the kinetics of this reaction has been obtained than hitherto by simultaneously measuring, as functions of time, the rate v_1 of reduction of the oxide,

$$\mathrm{MeO} + \mathrm{CO} = \mathrm{Me} + \mathrm{CO_2} \quad . \quad . \quad . \quad (1)$$

and the rate v_2 of the dissociation of CO,

$$2\mathrm{CO} = \mathrm{C} + \mathrm{CO_2} \quad . \quad . \quad . \quad . \quad (2)$$

The experimental technique used comprises the continuous, automatic measurement of the weight of a sample of oxide placed in a steady stream of CO, and also of the rates D_0, D_1 and D_2 of flow of the gases at the point of entry into the reaction chamber, at the exit of this chamber and at the exit of the CO_2 absorber placed after the reaction chamber respectively.

The weight of the sample is measured by means of a small oil-damped balance with a low centre of gravity enclosed in the gas-stream over the reaction chamber. This balance, constructed by Becker and Co., of Brussels has a beam 3·5 cm. long, and is capable of measuring differences in weight of about 0·5 g. to the nearest 0·001 g. The displacements from the equilibrium position of this balance are recorded on a photographic drum using the displacements of a beam of light reflected by a small mirror attached to the beam of the balance on its axis of rotation.

The gas flows are measured by small, electrically recording, phosphoric acid, bubble-type flowmeters. In these, the formation of a bubble interrupts an electrical circuit, and these interruptions are automatically recorded. Rates of flow up to 50 ml./min. are thereby measured with an accuracy of ± 0·1 ml./min. The weight of the sample of oxide is diminished by the loss of oxygen during the course of the reduction, but increased by the deposition of carbon produced by the dissociation of the carbon monoxide.

The rate of this dissociation is also directly proportional to the difference of the gas flows at the entry and exit of the reaction chamber ($v_2 = 2(D_0 - D_1)$), since this is the only reaction accompanied by a volume change of the gas. These two sets of measurements thus permit the calculation of the speeds, v_1 and v_2. The difference between the rates of flow at the entry and the exit of the CO_2 absorber, which is equal to the rate of formation of CO_2 by reactions (1) and (2), affords a check on the calculation of these speeds ($D_3 - D_2 = v_1 + v_2$).

The reduction of nickel oxide, NiO, and of ferric oxide, Fe_2O_3, has been studied by this method, using homogeneous samples weighing approximately 1·8 and 1·4 g. respectively, obtained by sintering the metallic oxides in powder form. The results for NiO are more easily interpreted, since the reduction of this oxide produces metallic nickel directly and because the nickel thus produced is less easily oxidised by CO_2 or carburised by CO than is iron.

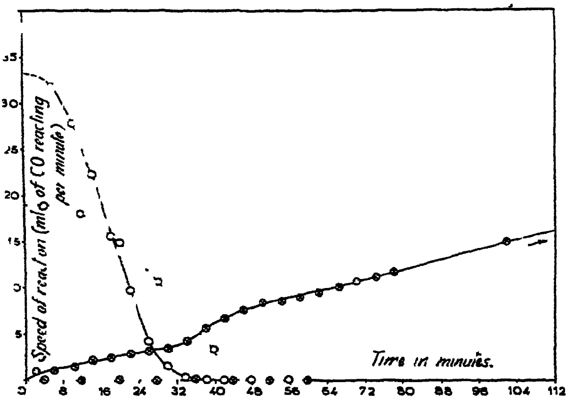

FIG. 1.—Reduction of NiO by CO at 600° c. with D_0 of CO or CO + CO_2 = 50 ml /min
By pure CO (full line) and by CO/CO_2 mixture (71/29) (dotted line).
Speed of reduction of oxide . . ○
Speed of dissociation of CO . . ⊕

Fig. 1 shows the variation of the speed of the reduction of NiO and of the Boudouard reaction at 600° ± 2° c. when reduction is carried out with pure CO (full curve) and with a $71CO/29CO_2$ mixture (broken curve). The rate of the reduction is found to vary in the same way as that observed in reactions taking place in the absence of the Boudouard reaction, as is the case, for example, in the reduction of copper oxide by CO.[1]

The dissociation of carbon monoxide begins at the onset of the reduction, increases in speed approximately linearly as this proceeds, accelerates towards the end of the reduction and increases approximately linearly once more when the reduction is complete. (In the experiment denoted by the full curve in Fig. 1, the speed of dissociation of CO was still accelerating linearly after 3 hr.). But the dissociation of CO is entirely stopped at 600° c. by the addition of approximately 30 % of CO_2, whereas, at this temperature, and with a total pressure of 1 atm., the $CO—CO_2$ mixture corresponding to the equilibrium position of reaction (2) contains about 75 % of CO_2.

More remarkable is the fact that the nickel thus reduced no longer induces the dissociation of carbon monoxide when placed in an atmosphere of this gas. In contrast to this, sponge Ni obtained by the reduction of an identical sample by hydrogen markedly catalyses the dissociation of CO, and the rate of dissociation increases with time, as with the reduction of NiO by pure CO. The Ni thus obtained entirely loses its activity when treated at 700° C. for 1 hr. in a stream of CO_2. The difference of these catalytic activities cannot be explained in terms of the poisoning of the Ni by an impurity in this gas, because Ni, already containing C, does not lose entirely its activity under this treatment.

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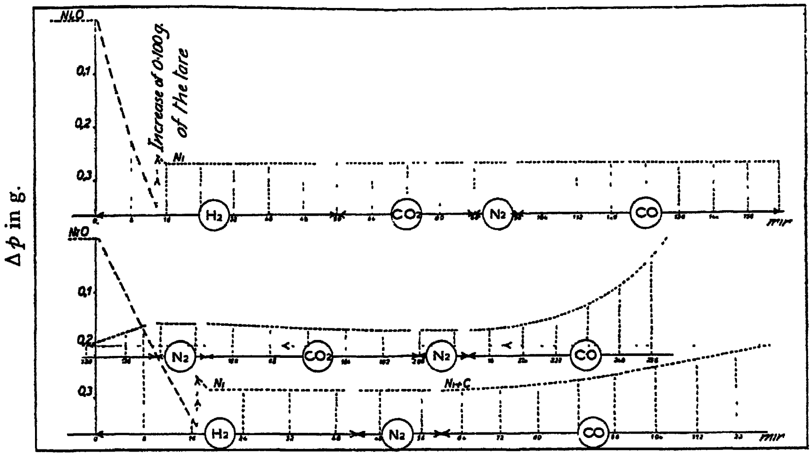
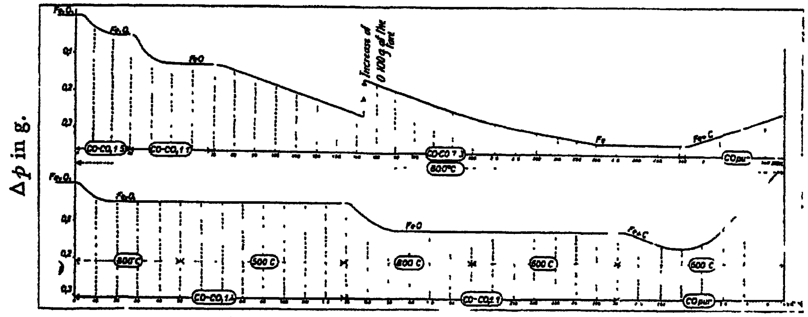
[1] cf. Juliard, *Bull. Soc. chim. Bel.*, 1932, **41**, 65, 138, 234 and 289.



Photographic record of the variation of the weight of a sample of 1·350 g. of NiO at 700° C. in a stream of various gases.



Photographic record of the variation of the weight of a sample of 1·320 g. of Fe_2O_3 at various temperatures in a stream of $CO + CO_2$ of various concentrations.

FIG. 2.

It is thus possible, by performing the reduction of NiO in an atmosphere of carbon monoxide containing sufficient CO_2, to prevent a subsequent occurrence of the Boudouard reaction, in conditions where the reaction is thermodynamically possible.

Fig. 3 shows the variation, under similar conditions (same number of g.-mol. oxide and same CO flow), of the rate of reduction and dissociation for the reduction of Fe_2O_3 by CO at 800° C. The reduction proceeds, in this case, in a slightly more complicated manner than for NiO, because of the successive steps :

$$Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe.$$

In this case the dissociation of CO does not begin immediately with reduction, because nearly all the available CO is consumed in the first two stages of this reduction (transformation of Fe_2O_3 to FeO).

By performing the reduction in stages at 800° c., using successively mixtures containing 20 % and 50 % of CO_2, it can be shown that the CO does not undergo dissociation so long as the sample of oxide does not contain any metallic iron (Fig. 2). The Boudouard reaction begins as soon as free Fe is formed and goes on, as with Ni, when the reduction is complete. In this experiment the rate of the Boudouard reaction remained approximately constant after complete reduction because it was limited by the equilibrium concentration of CO_2 imposed by reaction (2) (under a total pressure of 1 atm., the equilibrium concentration of CO_2 at 800° c. rises to approximately 10 %).

As in the case of Ni, Fe produced by the reduction of Fe_2O_3 by H_2 catalyses the Boudouard reaction, but it is not possible with this metal to eliminate the occluded hydrogen by oxidation with CO_2 since this gas simultaneously oxidises Fe, thus introducing a new promoter into the metal.

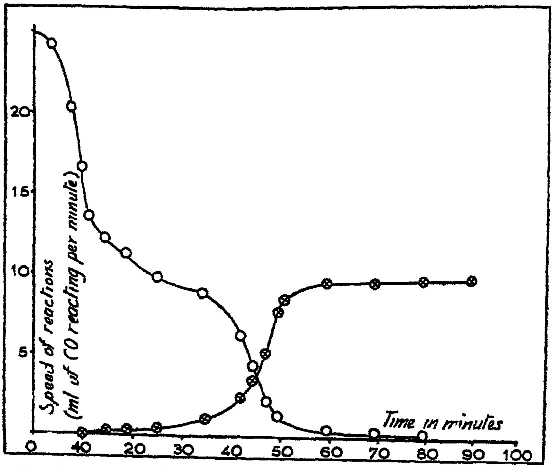


FIG. 3.—Reduction of Fe_2O_3 by CO at 800° c. with D_0 of CO = 50 ml./min.
Speed of reduction of oxide . . ○
Speed of dissociation of CO . . ⊗

Our experiments have shown that absolutely pure nickel does not catalyse the dissociation of carbon monoxide. On the contrary, nickel charged with hydrogen does catalyse this reaction; it takes place probably on account of carbon nuclei formed via the reduction of carbon monoxide by traces of active hydrogen adsorbed on the nickel crystallites.

With regard to iron and its oxides, we have observed that the Boudouard reaction does not occur in conditions such that metallic iron could not be formed. With iron we have always observed a catalytic activity, but this does not seem to be due to *pure* iron since in the circumstances used there was always a possibility of formation of FeO, Fe_3O_4 or Fe_3C.

In conclusion, it seems that the dissociation of carbon monoxide cannot start in contact with pure metal crystallites, but that it requires the presence of an interface like Ni-NiO or Fe-Fe_3C, or the prior formation of carbon nuclei.

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THE VAPOUR PRESSURE OF MAGNESIUM IN THE THERMAL REDUCTION OF MgO BY FERROSILICON

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Received 21st *July*, 1948

The production of magnesium metal by direct reduction of MgO has been carried out on a commercial scale in the United Kingdom, U.S.A., Canada and Australia. Two basic methods have been exploited—reduction of MgO by carbon, and reduction by a metal or metalloid, the oxide of which is non-volatile at the temperature of the operation.

The reduction of magnesium oxide by carbon follows the simple reaction.

$$MgO + C = CO + Mg(g) \quad . \quad . \quad . \quad . \quad (1)$$

It was shown by Slade[1] that the reaction would proceed to the right at temperatures of the order of 1900° c. Owing to the fact that the gaseous products would react at lower temperatures reforming MgO and carbon, the method was not employed commercially until the work of Hansgirg,[2] who developed a successful method of shock cooling the equilibrium mixture. The hot gaseous reaction products were blasted with a large excess of cold hydrogen. While the device is effective in suppressing the back reaction, it introduces a further complication in that the magnesium is condensed in the form of powder of submicroscopic particle size.[3] The powder is pyrophoric and cannot be coalesced by a melting operation. The only practical treatment for this dangerous material appears to be distillation, either *in vacuo* or in a stream of inert gas. A second step is thereby introduced and the simplicity of the basic reaction is, to some extent, sacrificed.

The carbon reduction or carbothermic process was first operated commercially in Korea. During the recent war, plants were built at Swansea, Wales, and at Permanente, California, U.S.A., the latter plant having a projected output of 12,000 short tons per annum. Both plants encountered numerous operating difficulties and apparently failed to obtain their rated output.

The second type of thermal reduction process avoids the difficulties inherent to the handling of reactive metal powders. In the reaction

$$MgO + X = XO + Mg(g) \quad . \quad . \quad . \quad (2)$$

if X and XO are non-volatile in comparison with magnesium, the reaction may be forced to the right by continuous removal of magnesium vapour. No other volatile vapours or gases are present in the system, and the magnesium may be collected in massive form.

In order that the reactions may proceed at reasonable velocity at moderate temperatures (1100°–1300° c.), reaction (2) must not be highly endothermic. The reducing agent X must preferably be a fairly reactive metal. While a number of feasible reducing agents are known, only three have been employed commercially—silicon, aluminium and calcium carbide. Silicon

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[1] Slade, *J. Chem. Soc.*, 1907, **93**, 327.
[2] Hansgirg, *German Pat.* 529,120, 1929.
[3] Dungan, *Trans. Amer. Inst. Min. Met. Eng.*, 1944.

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in the form of ferrosilicon was responsible for the largest production and was employed in U.S.A. and Canada in plants with an estimated annual output of 74,000 short tons.

The reaction of silicon is considered exclusively in this paper. The magnesia-bearing raw material is dolomite, which is chosen because it is available in unlimited quantities in a high state of purity, and is readily converted to a suitable form by simple removal of CO_2 by application of the lime-burners' traditional technique. The reduction reaction is considered to be

$$2MgO + 2CaO + Si(Fe) = 2CaO.SiO_2 + 2Mg(g) + (Fe) \quad . \quad (3)$$

The present authors have not proved the formation of the dicalcium silicate, but its existence is likely and has been frequently referred to by previous workers in this field.[4] No information was found in the literature on the Mg pressure over reaction (3). Mention has been made of the reaction :

$$2MgO + Si = 2Mg(g) + SiO_2 \quad . \quad . \quad . \quad (4)$$

Doerner[5] reports values calculated by Meier for reaction (4) as follows:

at 1200° C. : $P_{Mg} = 0{\cdot}190$ mm. Hg,

and at 1400° C. : $P_{Mg} = 0{\cdot}38$ mm. Hg.

On the basis of this calculation, Doerner concluded that reaction (4) did not offer attractive commercial possibilities.

The present work was almost completed when a paper by Schneider and Hesse[6] became available. These authors had used the experimental method to be described and had attempted to measure the equilibrium magnesium pressure over reaction (4). They reported a value of 1·9 mm. Hg at 1200° C., but concluded however that a magnesium orthosilicate had been formed. Experimental examination by one of the authors[7] of reaction (3) showed that the reaction was appreciable at 1050° C. and quite rapid at 1150° C. This information suggested that the reaction could be conducted in steel apparatus of simple design. A number of commercial plants were operated during the recent war using the silicon reduction of MgO and CaO at temperatures below 1200° C. The rapid distillation rates obtained in practice suggested that the magnesium vapour pressure is much higher in reaction (3) than that indicated for reaction (4).

The experiments to be described were conducted to determine the reaction pressure of reaction (3) between 1100° and 1200° C. With a measured value available for magnesium vapour pressure, the equilibrium constant is readily available and values ΔH and ΔG may be calculated.

Experimental

Since magnesium is the only vapour phase of appreciable magnitude over reaction (3), its magnitude is a measure of the equilibrium of the reaction. The experimental problem resolved itself into the measurement of its vapour pressure at temperatures of the order of 1200° C. A consideration of available methods showed that, with few exceptions, they may be separated, with respect to the principles involved, into static and dynamic systems.

Static methods involve some method of measuring the vapour pressure over the system at equilibrium. The Knudsen effusion method has been applied to a similar reaction producing calcium.[8]

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[4] Kroll, *Thermal Reduction of Alkaline Earth Metal Oxide* (Light Metals, Oct. 1944), p. 465. Grosvenor, *U.S. Pat.*

[5] Doerner, *U.S. Bur. Mines Bull.*, P, July, 1937

[6] Schneider and Hesse, *Z. Elektrochem.*, 1940, **46**, 24.

[7] Pidgeon, *Trans. Can. Inst. Min. Met.*, 1946, **49**, 621.

[8] Atkinson and Pidgeon, *Trans. Can. Inst. Min. Met.*, Jan., 1948.

In the case of the production of magnesium, the apparatus difficulties were less pronounced, owing to the lower reactivity of the metal vapour and the greater ease of condensation at high pressures. It was decided to adopt a dynamic method employing entrainment. A current of inert gas is passed through the sample until saturation is achieved. The metal vapours are condensed and weighed, and the volume of inert gas is also measured. From the known measured volume of inert gas and computed volume of metal, the vapour pressure of the latter may be obtained by application of the gas law.

The entrainment method is applicable to the pressure range which was expected It is least dependent on theoretical calculation and calibration. The apparatus is simple in construction and satisfactory accuracy and precision of measurement may be expected over a wide range of temperature.

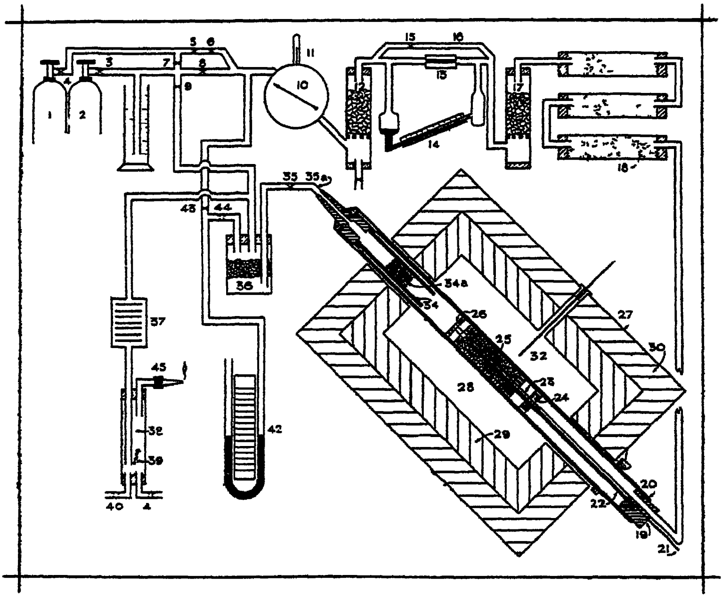

FIG. 1

The ideal conditions inherent to accuracy are :—

(1) Complete saturation of the carrier gas, which must itself be inert to magnesium, must be established throughout the measuring period. The reacting charge must not be appreciably depleted of reactants

(2) Temperature, pressure and rate of flow of reacting gas must be constant and accurately measured.

(3) Condensation of Mg must be complete, and the amount accurately determined.

(4) The reacting charge should be heated "instantly" to the reaction temperature and cooled instantly at the end of the measured period.

These are ideal conditions, some of which are impossible to fulfil in practice. Whenever departures from the ideal occurred, the effect of the discrepancy was determined and, if possible, a correction was applied.

Apparatus.—The apparatus is shown in Fig. 1. The carrier gas is commercial pressures are measured. Stopcock (6) is used to start and stop the hydrogen hydrogen (1) which passes through a regulator (4) where the tank and system flow which is set to a constant value by a regulating valve (5). Stopcocks (7, 8, 9) provide a means of purging the entire system with nitrogen before and after each run, to avoid explosive air-hydrogen mixtures.

The hydrogen passes through a wet test meter (10) where its volume is measured. The temperature of the hydrogen at the meter is registered on a thermometer (11). The hydrogen is then partially dried in a calcium chloride tower (12). Bypass tube (16) was employed to purge the system at high flow-rates. The hydrogen then passes through a calcium chloride drying tower (17) and a progression of tubes containing phosphoric pentoxide (18). Beyond the final drying tubes (18), the hydrogen enters the bottom end of the retort tube (20) through a tightly fitting rubber stopper (19). The hydrogen is heated on its way up the retort tube and passes through the briquetted reaction material (25). The reacting charge (25) is held in place by perforated iron plugs (24, 26) which are supported by a rod (22).

Magnesium vapours saturate the hydrogen in the reaction zone (25) and are carried to an iron tube condenser (34) containing a steel wool mesh (34*a*). The hydrogen leaves the upper end of the retort and passes through a dust trap (36) to a pulse eliminator (37), which removes the pulsation caused by the bubbling of the hydrogen in the back-pressure tube (38). The hydrogen, as it enters the back-pressure tube, is forced under an adjustable depth of water (39). The added back-pressure is registered on the manometer (42). The hydrogen leaves the back-pressure chamber through an orifice (45) where it is ignited.

The furnace (27) is mounted at an angle of 45° so that the reacting material will settle and completely fill the cross-sectional area of the retort tube. A close-fitting hole at each end of the furnace permits the retort tube to be slid in and out of the furnace. The furnace chamber (28) is lined with 2½″ of refractory brick (29) which is backed by 2½″ of insulating brick made of foliaceous mica (30). A Globar heating element rod is located on each side of the retort tube (20) and parallel to it. A chromel-alumel thermocouple (32), connected to the controlling pyrometer, was mounted with its hot junction ½″ to one side of the retort tube in the furnace chamber. This thermocouple is used only to control the temperature.

The retort tube (20) made of 28 % chromium steel is 35″ long with 1″ inside diam. and ⅛″ walls. The bore at the condenser end was slightly increased to form a shoulder upon which a lip at the top of the condenser could rest. The condenser (34), a 9″ length of soft iron pipe, was machined to give a close fit in the retort to prevent magnesium vapours from passing between it and the retort tube. A strip of steel wool (34*a*), weighing 1·000 g. and 4″ in length, fills the cross-sectional area of the condenser at the area where condensation takes place. A fresh piece of steel wool is used for each run.

A standard chromel-alumel thermocouple (21) in a 3/16″ iron protecting tube (23) projects through the centre of the briquetted charge (25) with its tip at the upper end of the reaction zone. The protecting tube extends beyond the bottom end of the reaction zone to prevent contamination of the thermocouple wires with magnesium vapours. Mounted in this manner, the thermocouple gives a measurement of the temperature of the reaction at the point where the magnesium vapours are leaving the reaction zone.

Reaction Mixture.—A Grenville series dolomite was obtained through the courtesy of Dominion Magnesium Limited. Its composition after calcination at 975° c. was as follows:

MgO = 44·00
CaO = 55·82
R_2O_3 = 0·24
Insol. = 0·32

The burned dolomite was ground in a Raymond impact mill to 90 % – 150 mesh. 78·8 ferrosilicon was ground to 100 % – 80 mesh with 30 % – 150 mesh. The reactants were mixed in stoichiometric proportions and briquetted without binders. The briquettes were lightly crushed and screened to produce a size range between – 0·371″ and + 0·185″. They were dried at 550° c for approximately 25 min.

Precision and Accuracy of Entrainment System.—It was realised that the degree of accuracy and precision obtained would depend on the ability of the entrainment system to fulfil the ideal conditions set forth above. Some 200 test runs were made during which certain sources of error were minimised or eliminated.

(*a*) SATURATION OF HYDROGEN WITH MAGNESIUM VAPOUR.—The fundamental principle of the system is that the carrier gas shall be saturated with magnesium vapour. This situation is achieved if the hydrogen after saturation passes over a portion of unreacted charge.

The reaction mixture must be long enough so that saturation has occurred before an appreciable fraction of the charge has been traversed. Obviously, the rate of hydrogen flow and length of the reaction mixture are interrelated. The reaction velocity is also a factor which is eliminated provided the reaction zone is long enough for a given hydrogen rate

Depletion of the charge takes place as the reaction proceeds, and this must not reach the end of the reaction zone. With a 40 g. charge, it was found that saturation could be maintained at hydrogen rates of 0·01 c. ft /min.; during the passage of 3 c. ft of H_2 approximately 2 g Mg were collected; weighing and handling losses should not exceed 0·001 g. which corresponded to 0·01 mm. Hg in the calculated vapour pressure.

The experimental conditions in this respect were notably different from those of Schneider and Hesse who apparently used a single briquette and made no attempt to achieve saturation, but relied upon extrapolation to zero hydrogen flow to give the saturation value. They reported reaction to the extent of 31 % at higher temperatures and indicated that different values were obtained when a briquette was re-treated. In the present work any effect due to reaction velocity has been completely eliminated (see Tables I and II).

TABLE I

THE EFFECT OF HYDROGEN RATE ON THE DEGREE OF SATURATION

Hydrogen Volume (c. ft. N.T.P.)	Hydrogen Rate (c. ft./min. at N.T.P.)	Condensed Magnesium (g.)	Apparent Reaction Pressure of Magnesium (P_{Mg}) (mm. Hg)
2·900	0·0388	2·192	18·3
2·900	0·0291	2·211	18·5
2·900	0·0193	2·223	18·6
2·900	0·0190	2·228	18·6
2·900	0·0096	2·232	18·7

(*b*) TEMPERATURE MEASUREMENT AND CONTROL.—Preliminary experiments showed that the reaction pressure almost doubled between 1100° and 1150° c., corresponding to a mean increase of 2 %/degree c. (0·4 mm Hg/degree c. at 1150° c.).

The controlling pyrometer permitted a period fluctuation of temperature in the furnace atmosphere at ± 1·5° c. The variation of the temperature in the centre of the reaction zone was barely detectable on a potentiometer reading to 0·25° c. The thermocouple in the reaction zone was viewed directly with an optical pyrometer after each run. If the E.M.F. of the thermocouple was found to be drifting, the thermocouple was renewed. Temperature gradients in the reaction zone were determined under operating conditions. The reaction zone was placed in a region of the retort in which the temperature was uniform to within 1° c.

TABLE II

Run No.	Vol. (c. ft. N.T.P.)	Rate (c. ft./min N.T.P.)	Condensed Magnesium (g.)	P_{Mg} (mm. Hg)
3	2·900	0·0290	2·228	18·6
4	2·900	0·0283	2·225	18·6
5	2·900	0·0192	2·233	18·7
2	2·900	0·0097	2·235	18·7

(*c*) HYDROGEN VOLUME MEASUREMENT.—Gas volumes were measured by a wet test meter accurate to 0·001 c. ft. The meter was calibrated by direct displacement methods. The wet test meter measures the volume of hydrogen used plus the volume of entrained water vapour from the hydrogen cylinder and the meter itself. For a number of tests at room temperature (24°–28° c.) a liquid-air trap was used to remove and collect the entrained water vapour. In several such tests the hydrogen was found to contain 3·3 ± 0·07 % by volume of water vapour.

Since the hydrogen/water vapour proportions remained so nearly constant, direct measurement of water content was abandoned and a standard correction was made for each experiment. A variation of 0·1 % by volume of water vapour in 3·000 c. ft of hydrogen introduces an approximate error of 0·01 mm. Hg in the reaction pressure measurement. The P_2O_5 drying train reduced water to less than 0·05 % corresponding to a pressure error of 0·005 mm. Any slight oxidising impurities in the hydrogen would be removed when the gas entered the reaction zone.

Atmospheric pressures in the laboratory varied between 740 and 765 mm. Hg. It was found preferable to use a constant pressure of 765 mm for all experiments. By checking the atmospheric pressure, frequently the total pressure could be held to within 0·5 mm. Hg by a simple adjustment of the back-pressure (see Fig. 1). The error so introduced is insignificant.

Since it is impossible to heat the sample instantly to the reaction temperature and cool it instantly at the end of the experiment, it was decided to use the hydrogen flow as a mechanism to initiate the measured period. A nominal H_2 flow of 0·0005 c. ft./min. was established with the tube outside the furnace, but charged and with the condenser in position. The furnace was brought to the operating temperature and the tube inserted. When the thermocouple in the charge read the required temperature, the desired hydrogen rate was established and the volume carefully measured. At the end of the measured period, the hydrogen rate was reduced to the nominal rate of 0·0005 c. ft./min. while the tube was removed from the furnace and cooled. The system was purged with nitrogen when it had fallen to 600° c. and subsequently opened when cool enough to handle.

A test run showed that only 0·0007 g Mg was produced during these heating and cooling periods introducing a negligible error of 0·005 mm Hg in the calculated vapour pressure.

(*d*) CONDENSATION OF MAGNESIUM VAPOUR.—During the early development of the apparatus, condensation of the magnesium vapours took place in an iron tube inserted in the retort tube to a point where a portion of its length was at the proper condensing temperature. With this arrangement, an average of about 15 % of the magnesium was condensing as powder. Depending on the hydrogen rate, from 10 to 20 % of this powder did not remain in the condenser and was difficult to collect. The powder was presumably formed by vapour-phase condensation, the magnesium vapour being condensed by the cold hydrogen in the vicinity of the condenser. The analogous case of Zn "blue powder" may be referred to.

The problem was solved by the use of a piece of steel wool in the condenser section. An extensive surface for condensation was provided, consequently powder formation was reduced to less than 0·1 % of the total weight of condensate. This powder was caught in the gauze so that losses by the escape of magnesium powder from the condenser were below the accuracy of the experiment.

The condensate was largely in the form of massive shiny crystals. An analysis of the deposit (courtesy of Dominion Magnesium Ltd.) is as follows:

$$\text{Al} < 0{\cdot}007\ \%,\ \text{Mn} < 0{\cdot}001\ \%,\ \text{Pb}\ 0{\cdot}01\ \%,\ \text{Ni} < 0{\cdot}0005\ \%,$$
$$\text{Cu} < 0{\cdot}0005\ \%,\ \text{Fe}\ 0{\cdot}031\ \%,\ \text{Si} < 0{\cdot}001\ \%,\ \text{Ca} < 0{\cdot}004\ \%.$$

(*e*) MAGNITUDE OF ERRORS.—The sum of the discernible errors, in terms of Mg pressure, is 0·02 mm. Hg. It seems reasonable to report values of vapour pressure to 0·1 mm. Hg

Results

Effect of Hydrogen Rate on p_{Mg}.—The initial experiments sought to prove that the entrainment gas was saturated with magnesium at the equilibrium pressure of the reaction

$$2\text{MgO} + 2\text{CaO} + (\text{Fe})\ \text{Si} = 2\text{Mg}(g) + 2\text{CaO.SiO}_2 + (\text{Fe})$$

at temperatures between 1100° and 1200° c. The rate of H_2 flow was widely varied and the corresponding equilibrium pressure calculated. Results appear in Table I.

The results plotted in Fig. 2 show a slight variation of apparent reaction pressure with gas velocity. The extrapolated pressure for zero flow was but 0·02 mm. Hg higher than that at 0·01 c. ft /min. This difference is within the experimental error and it is assumed that saturation was obtained at hydrogen flow rates of 0·01 c ft./min. or less. At rates much higher than 0·01 c. ft./min., saturation is not achieved in this system, and a longer reaction zone would be required.

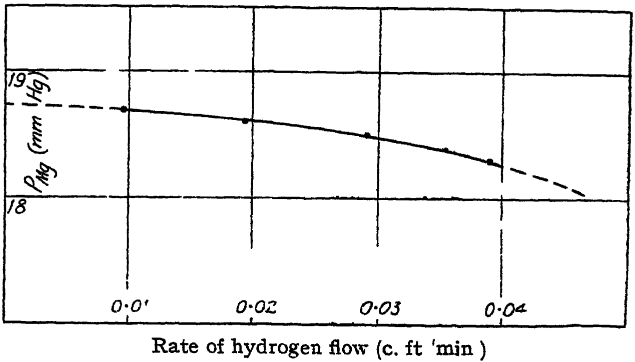

FIG 2.—Effect of the rate of hydrogen flow on the apparent reaction pressure at 1150° C.

Effect of CaF2 on Equilibrium Pressure Measurement.—It has long been known that CaF_2 accelerates reactions of this type.[9] If it acts as a catalyst, the equilibrium pressure should be unaffected. Results similar to those of Table I are shown in Table II. All conditions are the same, except for the addition of 5 % —200 mesh CaF_2, based upon the weight of the reacting charge.

The results appear in Table II. There is evidence of accelerated reaction rate as the apparent reaction pressures are higher at high rates of hydrogen flow. The extrapolated value at zero hydrogen flow is the same as that obtained in the absence of CaF_2.

Effect of Temperature.—The effect of temperature on pressure was determined by conducting similar experiments at temperatures between 1100° C. and 1190° C. At the highest temperature, the hydrogen rate and volume were reduced to prevent depletion of the reaction mixture. Results are shown in Table III.

TABLE III

Reaction Temp. ° C.	Hydrogen		Condensed Mg (g.)	P_{Mg} (mm. Hg)
	Rate (c. ft./min. N.T.P.)	Volume (c. ft. N.T.P.)		
1100	0·0099	2·900	1·192	10·1
1125	0·0096	2·900	1·670	14·1
1150	0·0096	2·900	2·232	18·7
1170	0·0085	1·455	1·450	24·0
1190	0·0045	1·353	1·715	30·2

The reaction pressures are plotted logarithmically in Fig. 3 producing a straight line which is expressed by the equation :

$$\log P_{Mg} = -\frac{10,875}{T} + 8{\cdot}918$$

Reaction pressures, calculated from this equation, and also covering a short range of temperature outside the experimental measurements, are shown in Table IV.

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[9] Kroll, *Light Metals*, Oct., 1944, p. 465.

Discussion

In reaction (4) magnesium is the only reactant as a product in the gaseous state. The equilibrium constant is therefore equal to the square of the magnesium pressure in atmospheres:

$$K_p = (P_{\mathrm{Mg}})^2.$$

Values of ln K plotted against $1/T$ yield a straight line from which it is possible to calculate the heat of reaction using the integrated form of the van't Hoft equation ·

$$\ln K = \frac{\Delta H}{RT}$$

TABLE IV

T (° K)	P_{Mg} (atm)	$K_p \times 10^4$	ΔH (cal)
1323	0·0065	0·433	100,970
1373	0·0120	1·722	100,340
1423	0·0250	6·250	99,670
1473	0·045	20·370	98,990
1523	0·080	61·915	98,300

Calculated values for K_p and ΔH appear in Table IV.

The magnesium pressure measured over reaction (4) is approximately ten times as high as that reported previously. The calculated value for ΔH is also smaller than expected. Calculated values for P_{Mg} obtained by selecting likely values for the entropies of the reactants and products give much lower values than those measured.

The experimental technique is fundamentally simple and few sources of error exist which would produce a high value. The use of a long reaction zone ensures that saturation was achieved in a manner independent of reaction velocity, and ensures supply of heat, and diffusion of magnesium to the surface of the briquette. This situation apparently did not exist in the experiments of previous workers who employed a single briquette. The previous work also employed a large excess of silicon (2MgO + Si), so that the probable reaction was

$$4\mathrm{MgO} + 2\mathrm{Si} = 2\mathrm{Mg} + 2\mathrm{MgO.SiO_2} + \mathrm{Si}.$$

In addition to this difference, the supply of magnesium vapour over the single briquette depended upon the reaction velocity and the diffusion of magnesium vapour to the surface of the briquette through the solid reaction products. These factors may account in part for the lower values reported by Schneider and Hesse.

The relatively high pressures of magnesium vapour which exist over the reaction mixture at temperatures of 1150° C. explain the good yields and rapid distillation rates which have been obtained commercially

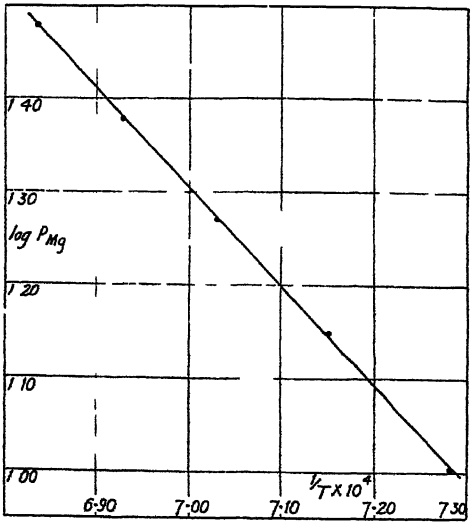

Fig 3

in heat-resisting steel apparatus. In full-scale operations in 10" retorts containing 200 lb. of charge, the total pressure had no effect on yields between 0·01 and 1·0 mm. Hg. Lower pressures (below 0·1 mm.) were desired to promote a dense condensate. Small-scale operations conducted by one of the authors [10] at various pressures of inert gas showed that the pressure could be increased to several mm. Hg before the yield was seriously reduced (P = 0·001 mm. Hg, yield = 78 %; P = 5 mm. Hg, yield = 72 %).

Mechanism of Reaction.—While the primary object of this work was the determination of the equilibrium vapour pressure, the apparatus was adaptable to qualitative experiments which indicated the nature of the reaction mechanism. At least three suggestions have been made, viz.,

(1) silicon vapour,[11]
(2) silicon monoxide (SiO)—Schneider and Hesse [12] held this view—and
(3) solid diffusion between the reactants of the system.

(1) and (2) postulate a volatile substance. Using the entrainment method, it should be possible to carry either of the gases from the reducing agent to the reactants. To determine the possible role of these reducing vapours, a charge of briquetted calcined dolomite was placed in a retort tube adjacent to, but separated from, granulated silicon (97 % Si) and heated to 1200° C. Hydrogen was first passed through the silicon to carry vapour, if any, to the area containing the briquetted dolomite. After 24 hr. only a negligible quantity of magnesium appeared in the condenser placed beyond the charges. Similar results were obtained when the silicon was replaced by a mixture of 10 % SiO_2 powder and 90 % granulated silicon. In contrast to this, intimate mixture of silicon with the dolomite causes complete reaction in but a few hours.

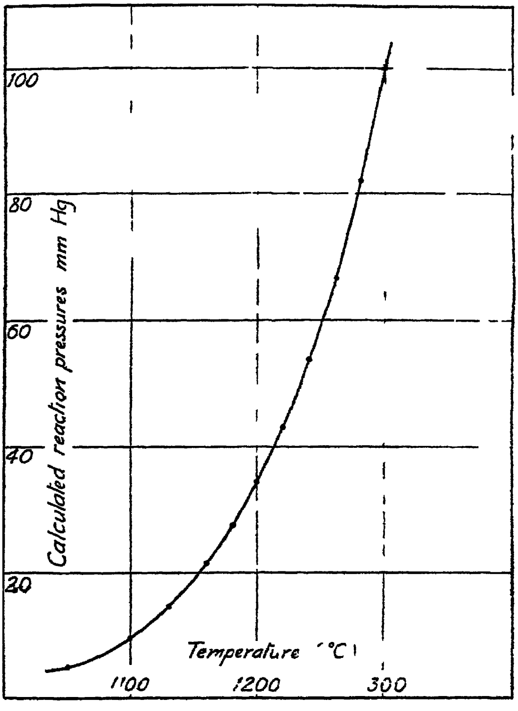

FIG 4.—Calculated reaction pressure curve for us extended range of temperature.

It appears, therefore, that SiO and silicon vapour have little or no function in the reaction at 1200° C. or less, but that the impetus stems primarily from solid diffusion between the reactants.

The authors wish to express their appreciation of the generosity of the

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[10] Pidgeon, *loc. cit.*

[11] Pidgeon, *loc. cit.*

[12] Schneider and Hesse, *loc cit.*

School of Engineering Research at the University of Toronto in supporting this investigation.

Summary

The equilibrium pressure of magnesium vapour over the system, 2MgO+2CaO+S (Fe), has been measured by the entrainment method at temperatures between 1100° and 1200° C. P_{Mg} was found to be much higher than was generally accepted. Using the P_{Mg} values established, K_p and ΔH were calculated for a range of temperature.

CaF_2 has no effect on the equilibrium vapour pressure, but is an effective catalyst for the reaction.

There is substantial evidence that such volatile reducing agents as silicon vapour and SiO are not a major factor in the reduction of MgO in this system. The high reaction rate is apparently supported by solid diffusion between the reactants.

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ON SOME EQUILIBRIA INVOLVING ALUMINIUM MONOHALIDES

By P. Gross, C. S. Campbell, P. J. C. Kent and D. L. Levi

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It has been proposed to refine aluminium, and to produce it from arc furnace products such as aluminium ferro-silicon, by utilising the formation of the normally unstable aluminium monohalides. If, for example,[1] aluminium trichloride vapour is passed over heated aluminium-bearing material, the equilibrium

$$2Al + AlCl_3 = 3AlCl \quad . \quad . \quad . \quad . \quad (1)$$

is approached, and the resulting vapour mixture reverts on cooling to pure aluminium and the normal halide, which is re-introduced into the process. The thermodynamics of the aluminium monohalides, and especially of the monochloride, is therefore of metallurgical interest.

All the aluminium monohalides are known from their band spectra. The spectroscopic data are sufficient for calculating the entropy of AlCl, and for making a satisfactory estimate of the entropy of AlF. They cannot, however, be used to give a reliable value for the heat of formation of these halides, since the energy of dissociation is uncertain because the transition cannot be identified without ambiguity, and quite apart from this, there is the unreliability inherent in the graphical Birge-Sponer extrapolation for molecules in which the ionic forces contribute appreciably to the binding. The heat of formation, therefore, must be determined from measurements of equilibria involving the monohalides, but because of the rather high temperatures involved, and the experimental difficulties arising from the very active nature of the aluminium monohalides, accurate heats of reaction cannot easily be determined from the temperature dependence of the equilibria. A more reliable value can be obtained from measurements of equilibria in which the free energies of all the other reactants are sufficiently well known, together with entropy values for the monohalides derived from band spectra.

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[1] *Brit. Pat.*, 582, 579.

The equilibrium

$$\mathrm{NaCl}(s) + \mathrm{Al}(l) = \mathrm{Na}(v) + \mathrm{AlCl}(v) \quad . \quad . \quad . \quad (2)$$

seemed suitable for this purpose provided that the simultaneous reaction

$$3\mathrm{NaCl} + \mathrm{Al} = \mathrm{AlCl_3} + 3\mathrm{Na} \quad . \quad . \quad . \quad (3)$$

occurred to only a negligible extent. This is shown to be the case by the equilibrium constants for reaction (1), determined in experiments described later in the paper, and could also be deduced from Miescher's[2] value of 5·35 ± 0·3 ev. for the dissociation energy of aluminium monochloride.

Direct measurement of the pressure of reaction (2) or of any similar reaction is difficult because the unstable halide reacts with the material of which any container, manometer, etc., might be constructed. For the measurements the following very simple experimental procedure, which appears to be of quite general application, was evolved. An unknown heterogeneous equilibrium, together with another known one (e.g., an evaporation) which must not interfere with the first, is allowed to establish itself in an evacuated vessel which is closed except for a capillary outlet. The equilibrium gas mixture streams through the capillary and is allowed to condense in a suitable condenser. The ratio of the unknown pressure to the known one is determined by analysis of the condensate after the experiment.

The condensate will be of the equilibrium composition if the dimensions of the capillary are so chosen that:

(*a*) the flow through the capillary is small compared with the mass of the molecules striking its cross-section per unit of time;
(*b*) the diameter of the capillary is great compared with the mean free path; and
(*c*) the flow through the capillary is small enough not to upset equilibrium inside the vessel, and great enough to make the effect of any back-diffusion into the vessel negligible.

In order to test this method, experiments were carried out comparing the vapour pressure of potassium chloride (solid) with that of lead (liquid), the results yielding satisfactory values for the heat of evaporation of lead. By comparing the pressure of reaction (2) with the vapour pressure of sodium chloride, the heat of formation of aluminium monochloride was derived. Comparison of the pressure of the reaction

$$\mathrm{KCl}(s) + \mathrm{Al}(l) = \mathrm{K}(v) + \mathrm{AlCl}(v) \quad . \quad . \quad . \quad (4)$$

with the vapour pressure of potassium chloride, enabled a second value for this heat of formation to be calculated. By comparing the pressure of lead with the pressure of the reaction

$$2\mathrm{Al} + \mathrm{AlF_3} = 3\mathrm{AlF} \quad . \quad . \quad . \quad . \quad (5)$$

a value for the heat of formation of aluminium monofluoride was obtained.

Finally, the equilibrium constant of reaction (1) was measured directly at temperatures in the region of 1000° C. and at pressures of about 25 mm. of aluminium trichloride. The method used involved the passing of a known volume of purified argon over heated solid aluminium trichloride (thereby establishing a definite partial pressure of aluminium trichloride) and then bubbling the gas through liquid aluminium at a known rate. Equilibrium was established, and the equilibrium mixture formed was passed over a copper gauze in which the following reaction occurs:

$$3\mathrm{AlCl} + \mathrm{Cu} = \mathrm{AlCl_3} + (\mathrm{Al}, \mathrm{Cu}).$$

Aluminium trichloride is reformed, and the aluminium alloys with the copper.

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[2] Miescher, *Helv. physic. Acta*, 1935, **8**, 279.

This gives a method of estimating the concentration of monochloride in the original equilibrium mixture by determining the aluminium content of the copper analytically.

Experimental

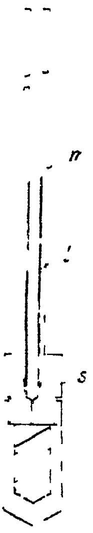

FIG. 1.

The vessel (Fig. 1) used for the comparison of the vapour pressures was made either from graphite or from pure alumina sintered to such an extent that it was gas-tight but still machineable.* The graphite vessel (3 in.–5 in. long and 1 in.–2 in. external diam.) was machined from a rod and threaded to take a screwed-in stopper (*s*). The alumina vessel (3 in. long and 1⅜ in. external diam.) had a ground-in alumina stopper. The stoppers had a drilled capillary outlet and a recess to take a ground-in refractory (mullite) tube (*m*).

Three sizes of capillary were used, the nominal dimensions of which were: (*a*) length 5 mm., diam. 0·343 mm. (80 Morse); (*b*) length 12·5 mm., diam. 1·75 mm.; (*c*) length 12·5 mm., diam. 3·5 mm. The refractory tube (length 45 cm.) served as the condenser, two sizes of bore being used, (N) 7 mm. and (W) 15 mm. In the experiments in which aluminium was distilled it was absorbed by a metal lining (generally copper †) inside the refractory tube.

The vessel was filled, in the case of the lead-potassium chloride experiments, with a mixture of A.R. lead powder and fused A.R. potassium chloride which had been coarsely crushed and sieved. In the experiments with solid sodium or potassium chloride and aluminium, coarse aluminium powder was mixed with granules obtained by sieving coarsely crushed briquettes made from fine aluminium powder and fused A.R. halides. In the experiments with liquid salts, coarse aluminium powder was supported by coarse alumina powder and the salt was contained in a small alumina boat into which it had been fused.

The filled reaction vessel, with the condenser attached, was placed inside a silica tube which itself was for half its length put into a tubular furnace. The vessel itself was situated in the hot zone of the furnace, the mullite tube extending into the cold unheated part of the silica tube. The silica tube was evacuated and kept at constant temperature for a suitable time, the temperature being measured and controlled by a platinum–platinum-rhodium thermocouple attached to the outside of the tube. The measured temperature was corrected for the temperature difference between the outside and inside of the tube.

In the case of the lead-potassium chloride, the aluminium-sodium chloride and the aluminium-potassium chloride systems, the temperature dependence of the two pressures compared is about the same. This has the advantage of making it unnecessary to measure the temperature with very great accuracy. The temperature dependence of the ratio of the vapour pressure of lead to the pressure of reaction (5) is greater than that for the corresponding ratio in the other systems studied, but it is much smaller than the temperature dependence of the pressure of reaction (5) itself.

After the experiments the mullite tube was removed from the vessel, and the condensate analysed. For the lead-potassium chloride series, where no lining was used, the potassium chloride was dissolved in hot water, the solution filtered and the potassium chloride in the filtrate titrated. The condensed lead which remained inside the tube and any traces which might have washed off during solution of the potassium chloride and remained as residue after filtration were dissolved in nitric acid and determined as chromate.

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* The alumina vessel was used to exclude any possible interference by the formation of aluminium carbide. This would be the case only if carbide were formed much more readily than aluminium monohalide, but in spite of the flow rate, using graphite, being changed by a factor of 9, no trend in the ratio Al/NaCl was observed.

† We are indebted to Dr. W. E. Alkins, of Messrs. Thomas Bolton and Sons Ltd., for supplying some of the oxygen-free high-conductivity copper foil.

In the experiments in the sodium chloride-aluminium and potassium chloride-aluminium series, a short copper lining was used. This was removed from the tube and the condensed halide dissolved in water and determined by titration. The lining itself was dissolved in nitric acid, the copper removed from solution by electrolysis, and the aluminium determined by precipitation with ammonia and weighing as Al_2O_3

In a few experiments with liquid salt a nickel lining had been used, the aluminium content being determined by weight difference. This procedure was less satisfactory.

In the aluminium fluoride-lead-aluminium series, the weight of the aluminium fluoride was determined by direct weighing after collecting it carefully from the unrolled lining. The lead was deposited in the cooler region of the copper lining. This portion of the lining was dissolved in acid and the lead estimated as chromate after removal of copper by electrolysis. That lead which condensed with the fluoride was estimated separately. The aluminium was absorbed in the hottest zone of the lining and was estimated as already described.

In the experiments for the direct determination of the equilibrium constant of reaction (1), the apparatus was as follows. Argon of 99·1 % purity, supplied from a cylinder, was used. It passed through a flowmeter and then through a purification train consisting of (1) a tube containing magnesium perchlorate, (2) a phosphorus pentoxide tube, (3) a tube containing copper gauze heated to 700° c. (to remove oxygen), (4) a tube containing calcium turnings heated to 750° c. (to remove nitrogen), (5) two tubes containing phosphorus pentoxide. The gas then passed through a glass tube about 12 in. long and of ½ in. bore, containing vacuum-redistilled aluminium trichloride. The tube was placed in a thermostat kept at a temperature in the region of 125° c. and constant to ± 0·1° c. After saturation with aluminium trichloride the gas passed through the heated glass tube (*g*, Fig. 2) and then through the alumina tube (*a*), which dipped into liquid aluminium (*l*). The glass tube was connected to the alumina tube by means of a cone-and-socket joint (*j*) which was lubricated with a mixture of graphite powder and silicone grease; this joint was gas-tight when kept at 140° c. The liquid aluminium was in the inner alumina tube (*i*), which itself was inside a larger alumina tube (*o*). At the top of the tube (*i*) was a system of alumina baffles (*b*), which prevented the molten metal from splashing on to the copper gauze (*cg*) placed above the baffles. The alumina tube (*o*) was inside the silica tube (*s*), which was surrounded by an electric furnace. The top of the silica tube was sealed off from the air by a packing of alumina powder (*p*) which, however, was sufficiently porous to permit escape of the argon after it had passed over the copper gauze. Since the stream of gas through the liquid was comparatively slow (about 3 l./hr.), a further stream of purified argon (12 l./hr.) was passed into the top of the silica tube so as to sweep away any air that might have diffused in. This second stream also escaped through the alumina packing. The upper part of the silica tube contained a roll of copper gauze (*c*) which offered an additional means of removing oxygen which might have diffused in. The absence of oxygen from the system was essential in these measurements, since it might have reacted with aluminium monochloride and so have reduced the apparent concentration of the latter. A thermocouple

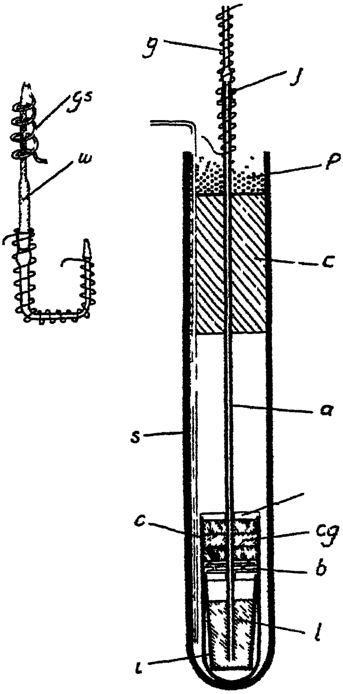

FIG. 2.

(not shown) was used to measure the temperature of the middle of the column of liquid aluminium, the total temperature gradient of which did not exceed about 4° c. The temperature gradient in the furnace was such that there was a rise in temperature between the surface of the aluminium and the copper gauze (*cg*). This prevented any partial reversal of the reaction by cooling of the equilibrium mixture before it had passed over the copper gauze. The copper gauze was in three sections, each about ¼ in. high The bottom gauze absorbed about 98 % of the total aluminium found, showing that this method of estimation is practically quantitative.

It was found impossible, at the gas flow rates used, to obtain reproducible values for the partial pressure of aluminium trichloride by relying on saturation of the argon at a known temperature of the trichloride. Consequently, after each run, the composition of the gas was estimated by condensing the trichloride on the walls of a weighed glass spiral (*gs*) connected to the tube (*g*) by means of a ground joint attached to (*j*). Since aluminium trichloride shows a very marked tendency to supersaturation, quantitative condensation by this method was possible only when the glass wall had been previously etched with hydrofluoric acid, and when in addition the spiral contained a packing of glass wool (*w*) similarly etched. This method of analysis gave results reproducible to 2 %.

In the experiments the whole apparatus was first thoroughly swept out with argon, the electric furnace and the aluminium trichloride thermostat then being brought to the required temperature. For the measurements about 3 l. of argon was used, the volume being read (to 0·1 %) by means of an aspirator system. The temperature and pressure of the gas were also read. After a sufficient volume had passed, the furnace was allowed to cool with the secondary argon stream still running. An estimation of the trichloride content of the primary argon stream was then made. Finally the aluminium content of the copper gauze (*cg*) was determined analytically.

TABLE I

THE SYSTEM LEAD-POTASSIUM CHLORIDE (SOLID)

Graphite vessel, temperature 748° c.

Stopper Type	Condenser Tube	Time (hr.)	Lead (g.)	KCl (g.)	Mole ratio Pb/KCl
C	W	3	0·349	2·035	0·0624
C	W	3	0·318	1·834	0·0629
C	N	3	0·230	1·279	0·0653
C	N	3	0·199	1·083	0·0668
B	W	6	0·114	0·712	0·0582
B	W	6	0·129	0·738	0·0635
B	W	6	0·127	0·718	0·0643
B	W	6	0·108	0·606	0·0648
B	N	6	0·092	0·533	0·0626
B	N	6	0·087	0·509	0·0623
				Mean value adopted =	0·0633

Condenser Tube, W bore = 15 mm.; N bore = 7–8 mm.

Stopper Type: C, Capillary 3·5 mm. nominal bore × 12·5 mm.
B, Capillary 1·75 mm. nominal bore × 12·5 mm.

Results

The consistency of the experiments with solid salts, as seen from Tables I, II and IV, was in general satisfactory, especially if one considers the variations (0·1 to 0·8 g./hr., Table I, 0·022 to 0·48 g./hr., Table II) in the rate of flow of vapour through the capillary. In the experiments with lead-aluminium trifluoride without aluminium, which were made with the intention of redetermining the vapour pressure of aluminium trifluoride independently, the results were much less reproducible and too low. This may have been due to the vapour of the trifluoride, like that of aluminium trichloride, tending to be supercooled and thereby escaping from the condenser. The ratio of aluminium trifluoride to lead was much more reproducible in the experiments with aluminium. This may have been due to the formation of crystallisation centres by the reversal of reaction (5).

TABLE II

THE SYSTEM ALUMINIUM-SODIUM CHLORIDE (SOLID)

Graphite vessel, temperature 780° c.

Stopper Type	Time (hr.)	Aluminium (mg.)	Total NaCl (g.)	Mole ratio Al/NaCl*
C	2·25	28·25	1·052	0·0617
C	2	23·5	0·781	0·0702
C	2	20·8	0·758	0·0632
B	6	9·0	0·334	0·0617
B	6	10·2	0·379	0·0621
B	6	8·1	0·305	0·0611
B	6	8·65	0·316	0·0630
B	6	8·85	0·313	0·0651
Alumina vessel, temperature 760° c.				
B	18	10·3	0·388	0·0609
B	18	10·4	0·385	0·0624
B	18	11·2	0·415	0·0616
B	18	10·8	0·459	0·0547
			Mean value adopted =	0·0623

Stopper Type : C, Capillary 3·5 mm nominal bore × 12·5 mm.
B, Capillary 1·75 mm. nominal bore × 12·5 mm.

* This refers to salt distilled by direct evaporation only.

The results of the experiments with liquid sodium chloride given in Table III were obtained in a series of five consecutive runs. Other series with liquid sodium chloride, although not seriously affecting the average, showed rather erratic deviations. Similarly, less satisfactory results were obtained when using liquid potassium chloride with lead at 970° c. in graphite, stainless iron, and leaded mild steel vessels. The deviations may be connected with surface action in the capillaries, since higher results were obtained with a mild steel vessel (wetted by both liquid lead and liquid salt) than with either the oxidised stainless steel vessel (wetted only by salt) or the graphite vessel (wetted only by salt, and in addition able to absorb appreciable amounts of liquid salt).

TABLE III

THE SYSTEM ALUMINIUM-SODIUM CHLORIDE (LIQUID)

Graphite vessel ; capillary of nominal bore 0·343 mm., length 5 mm.

Time (hr.)	Temp. ° c.	Aluminium (mg.)	Total NaCl (g.)	Mole ratio Al/NaCl*
3	970	44·8	1·072	0·0995
2·25	960	21·8	0·496	0·1052
2	970	15·0	0·345	0·1040
2	970	15·8	0·337	0·1131
2	970	12·4	0·288	0·1031
			Mean value adopted =	0·1050

* This refers to salt distilled by direct evaporation only.

The direct measurements of the equilibrium constant for reaction (1) gave satisfactorily reproducible results, shown in Table V.

The System Lead-Aluminium-Aluminium Fluoride.—Nine experiments on the equilibrium between aluminium and aluminium trifluoride, using lead as comparison substance, were carried out at 920° c. in a graphite vessel. About 0·200 g. of aluminium trifluoride distilled in 2 hr., the average weight ratio Al/Pb being 1·49, with a standard deviation of 0·13. The average ratio of the weight of trifluoride distilled by direct evaporation to that of lead was 2·38, the standard deviation being 0·12.

TABLE IV

THE SYSTEM ALUMINIUM-POTASSIUM CHLORIDE (SOLID)

Graphite vessel, temperature 750° c. Capillary 3·5 mm.; nominal bore × 12·5 mm.

Time (hr.)	Aluminium (mg.)	Total KCl (g.)	Mole ratio Al/KCl *
2	4·75	0·841	0·0158
2	5·8	0·960	0·0168
2	4·3	0·680	0·0178
		Mean value adopted =	0·0168

* This refers to salt distilled by direct evaporation only.

TABLE V

THE SYSTEM ALUMINIUM-ALUMINIUM TRICHLORIDE (GAS)

Aluminium distilled (mg.)	Pressure mm. (Hg)	Temperature ° C.	α %	φ	ΔG°_{1250}
99·5	26·3	1005	25·2	15·0	20,150
43·4	22·4	985	21·2	6·1	20,890
57·9	28·2	976	22·7	12·1	18,560
55·8	16·6	996	25·0	5·8	21,870
75·9	14·8	1005	28·0	7·4	21,940
30·8	12·0	952	25·4	3·2	19,940
29·6	15·3	965	19·3	2·2	21,810

α is the fraction of aluminium trichloride converted to monochloride; φ is the quantity $\frac{\alpha^2 p^2}{1-\alpha}$ and is equal to $\frac{(760)^2 K_p}{27}$, p being in mm.

Discussion

For comparing the results with each other and with previous values, the thermodynamic data and formulæ shown in Table VI were used.

A. The Lead-Potassium Chloride System.—Reliable vapour pressure measurements on potassium chloride were carried out by Fiock and Rodebush[18] and by Niwa.[15] Our own experiments were carried out at a temperature between the temperatures used by these two investigators. Vapour pressure measurements of lead at about the same temperature as our own were carried out by Egerton[19] and Fischer.[17] If the heat of evaporation of lead at 25° c. is calculated with their data one obtains

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[15] Kelley.[9] Using the vapour pressure data of Niwa, *J. Chem. Soc., Japan*, 1938, **59**, 637, the free energy of evaporation is less by 1770–1·36*T*.

[17] Fischer, *Festsch. Tech. Hochschule Breslau*, 1935, 172.

[18] Fiock and Rodebush, *J. Amer. Chem. Soc.*, 1926, **48**, 2522.

[19] Egerton, *Proc. Roy Soc. A*, 1923, **103**, 469.

TABLE VI

THERMODYNAMIC DATA

Substance	ΔH°_{298} cal.	S°_{298} cal./degree	C_p cal./degree	Other data
$Al_{(solid)}$	0	6·75[3]	$4{\cdot}80 + 3{\cdot}22 \quad 10^{-3}T$[4]	$\lambda_m = 2550$ cal.[5] Al_{liquid} : $C_p = 7{\cdot}00$[4] M.p. = 931·7° K.
$AlCl_{3(solid)}$	− 167,900[6]			$\lambda_{(subl.)} = 28{,}848$ cal.[7] $D(Al_2Cl_6 = 2AlCl_3) = 29{,}000$[8]
$AlCl_{3(gas)}$	− 138,575	74·63[9]	$7{\cdot}94 + C_{vib.}$*	$I = 370{\cdot}10^{-40}$ g. cm.[2] †
$AlF_{3(solid)}$	− 329,000[10]	12·5[11]	$18{\cdot}58 + 560{\cdot}0 \times 10^{-5}T - 179{\cdot}0 \times 10^{3}.T^{-2}$[12]	
$NaCl_{(solid)}$	− 98,330[10]	17·3[3]	$10{\cdot}79 + 4{\cdot}20 \times 10^{-3}T$[4]	$\lambda_m = 7220$ cal.[5] $NaCl_{liquid}$: $C_p = 15{\cdot}9$[4] M.p. = 1073° K.
$KCl_{(solid)}$	− 104,361[10]	19·76[3]	$10{\cdot}93 + 3{\cdot}76 \times 10^{-3}T$[4]	
$Na_{(gas)}$	25,950[7]	36·72[3]	4·97	
$K_{(gas)}$	21,520[7]	38·30[3]	4·97	
AlCl	—	54·18[9]	$6{\cdot}95 + C_{vib.}$[13]	
AlF	—	51·55[9]	$6{\cdot}95 + C_{vib.}$[14]	
$NaCl_{(solid)}$	$\Delta G_{evap} = 56{,}960 - 52{\cdot}32T + 2{\cdot}10 \times 10^{-3}T^2 + 4{\cdot}12T \log T$ $\Delta H_{evap.} = 56{,}960 - 1{\cdot}79T - 2{\cdot}10 \times 10^{-3}T^2$ [15]			
$NaCl_{(liquid)}$	$\Delta G_{evap.} = 52{,}800 + 15{\cdot}9\,T \log T - 81{\cdot}89T$ $\Delta H_{evap.} = 52{,}800 - 6{\cdot}9\,T$ [7]			
$KCl_{(solid)}$	$\Delta G_{evap.} = 53{,}770 - 51{\cdot}85T + 1{\cdot}88 \times 10^{-3}T^2 + 4{\cdot}44\,T \log T$ $\Delta H_{evap.} = 53{,}770 - 1{\cdot}93\,T - 1{\cdot}88 \times 10^{-3}T^2$ [16]			
$Pb_{(liquid)}$	1. $\Delta G_{evap.} = 45{,}750 - 36{\cdot}59\,T + 4{\cdot}21\,T \log T$[7] 2. $\Delta G_{evap.} = 47{,}020 - 39{\cdot}11\,T + 4{\cdot}80\,T \log T$[17]			

[3] Kelley, *U.S. Bur. Mines Bull.*, 434.

[4] Kelley, *U.S. Bur. Mines Bull.*, 371.

[5] Kelley, *U.S. Bur. Mines Bull.*, 393.

[6] Roth and Büchner, *Z. Elektrochem.*, 1934, **40**, 89.

[7] Kelley, *U.S. Bur. Mines Bull.*, 383.

[8] Calculated from Fischer, *Z. anorg. Chem.*, 1931 **200**, 332.

[9] Calculated from Sackur-Tetrode formula.

[10] Rossini and Bichowsky, *The Thermochemistry of Chemical Substances* (New York, 1936).

[11] Estimated from similar molecules and the vapour pressure constant of Ruff and Le Boucher, *Z. anorg. Chem.*, 1934, **219**, 376.

[12] After Pearson and Waddington, *Faraday Soc. Discussions*, 1947, **1**, 308.

[13] $\omega = 481$ cm.$^{-1}$, $I = 116{\cdot}10^{-40}$ g. cm.^{2} Herzberg, *Molecular Spectra and Molecular Structure, Diatomic Molecules* (New York, 1939), p. 483.

[14] $\omega = 815$ cm.$^{-1}$, Rochester, *Physic. Rev.*, 1939, **56**, 304. $I = 53{\cdot}5.10^{-40}$ g. cm.^{2} The interatomic distance was estimated from MgF and SiF, and AlCl.

[16] Kelley.[9] Using Niwa's data the free energy of evaporation is less by 1760—2·30T.

* This has been calculated assuming $\omega = 200$ (3) and $\omega = 500$ (3). The values for the frequencies have been arrived at by comparing similar molecules.

† $\bar{I} = (I_1I_2I_3)^{1/3}$. The known values for I^3 of all molecules of the type ACl_3 (or AF_3) lie on straight lines when plotted against the atomic weight of the central atom. σ is assumed to be 3.

46,360 cal. and 46,615 cal. respectively. According to whether the potassium chloride vapour pressures of Fiock and Rodebush or Niwa are accepted, the heat of evaporation of lead arrived at from our own experiments is 46,470 or 47,060 cal. This agreement must be considered very satisfactory.

B. The Aluminium-Sodium Chloride (Solid) System.—Using the experimental values of the equilibrium constant for reaction (1) together with entropy data in Table VI, it is easily shown that reaction (3) contributes only a negligible amount (less than 0·1 %) of the distilled aluminium in each series with sodium or potassium chloride; it is, therefore, neglected in all the calculations. Taking the mean value for the standard free energy of evaporation of the sodium chloride derived from Fiock and Rodebush and Niwa, and the values of Tables II and VI, the standard heat of formation (ΔH°_{298}) of aluminium monochloride is − 11,350 cal. The uncertainty brought about by the difference in the vapour pressure data for sodium chloride is ± 180 cal.

C. The Aluminium-Sodium Chloride (Liquid) System.—Taking Fiock and Rodebush's vapour pressure data (which cover our experimental temperature) and the values of Table VI for the other data, we find for aluminium monochloride $\Delta H^\circ_{298} = -12{,}120$ cal.

D. The Aluminium-Potassium Chloride (Solid) System.—Taking Fiock and Rodebush's vapour pressure data for potassium chloride and other data from Table VI, $\Delta H^\circ_{298} = -11{,}790$ cal. The weighted mean of all three determinations for ΔH°_{298} is − 11·58 kcal. Taking the heat of dissociation of chlorine $D_{Cl_2} = 56{\cdot}9$ kcal.[10] and the heat of evaporation of aluminium as 77·10 kcal.,[20] one arrives at 5·06 ev. for the dissociation energy of aluminium monochloride.

E. The Lead-Aluminium-Aluminium Trifluoride System.—Combining the average of the free energy of evaporation of lead obtained from Kelley[7] and Fischer[17] with our own experimental data, one obtains a vapour pressure for aluminium trifluoride at 1193° K. of 2·45 mm. if the vapour is monomeric, and of 1·23 mm. if it is dimeric. These values are in good agreement with the value of 1·48 mm. derived from Narishin's[21] measurements. Narishin's values, determined in the temperature range from 1025° K. to 1270° K., are compatible with the measurements of Ruff and Le Boucher[22] and Olbrich[23] (both in the temperature range 1370°–1550° K. and using the same method), if it is assumed that the vapour is dimeric at lower temperatures and begins to dissociate at about 1150° K. Taking the average of Kelley's and Fischer's vapour pressure formulæ, the data of Table VI, and the measured ratio of aluminium to lead, the standard heat of formation of aluminium monofluoride is − 49,720 cal. The lower value for the heat of formation of the trifluoride estimated by Roth[24] (236 kcal. for AlF_3 gas) would reduce this by about 6 kcal. An error of 5 units in our estimated entropy of $AlF_{3\,\mathrm{solid}}$ would involve a change of only 2 kcal. Taking Gaydon's[25] value for the dissociation energy of F_2 (2·2 ev.) one arrives at 7 ev. for the dissociation energy of aluminium monofluoride.

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[20] Eucken, *Metallwirt*, 1936, **15**, 63.
[21] Narishin, *J. Physic. Chem. U.R.S.S.*, 1939, **13**, 528; *A.C.S. Abst.*, 1940, **37** 1237.
[22] Ruff and Le Boucher, *Z. anorg. Chem.*, 1934, **219**, 376.
[23] Olbrich in Gmelin's *Handbuch der anorg. Chemie* (Aluminium B.I.), p. 160.
[24] Roth, *Ber. B*, 1937, **70**, 48.
[25] Gaydon *Dissociation Energies and Spectra of Diatomic Molecules* (London 947). p. 208.

F. The Aluminium-Aluminium Trichloride System.—The free energy at 1250° K. for reaction (1) found from the experiments is + 20,740 cal. Using the found value for the heat of formation of aluminium monochloride and the values of Table VI, we obtain $\Delta G = 92{,}940 - 61{\cdot}20T$ for the free energy of reaction (1) in the region of 1250° K. This gives a value of + 16,620 cal. for ΔG°_{1250}. This agreement must be considered very satisfactory, since the difference can easily be accounted for by the uncertainty in the thermochemical data, and especially in the entropy of $AlCl_3$. It is, however, possible that equilibrium for reaction (1) was not quite reached.

We are indebted to the Directors of Messrs. International Alloys Ltd., on whose behalf the investigation was carried out at this Institute, for their consistent support and for permission to publish these results. We are very grateful to Mrs. M. P. Campbell and Mr. J. A. McBain for invaluable assistance throughout the investigation, and to our colleague Mr. E. A. Brandes for making the alumina ware for this work.

Summary

A simple method of determining vapour or reaction pressures by comparing them with a known equilibrium pressure, such as a vapour pressure, is described. The reliability of the method was established by comparing the vapour pressures of lead and potassium chloride.

The method was used to determine the reaction pressures of $Al + NaCl = Na(v) + AlCl(v)$ and $Al + KCl = K(v) + AlCl(v)$. From these pressures and the entropy of AlCl, obtained from spectroscopic data, the heat of formation of AlCl was derived $\Delta H^\circ_{298} = -11{\cdot}5_8$ kcal.).

Some experiments were carried out by the same method to determine the reaction pressure of $2Al(l) + AlF_3 = 3AlF(v)$, and to derive from it the heat of formation of $AlF(\Delta H^\circ_{298} = -49$ kcal.).

The equilibrium of the reaction $2Al(l) + AlCl_3 = 3AlCl$ was determined directly by a transference method and satisfactory agreement between calculated and experimental values found.

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THE REDUCTION OF ZINC SULPHIDE BY IRON UNDER REDUCED PRESSURE

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The direct reduction of zinc sulphide by iron was proposed some time ago and more recently has been the subject of a careful thermodynamic investigation by Kelley.[1] Hitherto the equilibrium considered has been that between a liquid phase containing zinc sulphide, iron and iron sulphide, and a vapour phase consisting essentially of zinc vapour under 1 atm. pressure. In order to displace the equilibrium in the liquid phase far enough, rather high temperatures are necessary.

If the temperature of the system is, however, reduced below the eutectic temperature (1188° C.) of the zinc sulphide-iron sulphide system, the

[1] Kelley, *U.S. Bur. Mines Bull.*, 1937, 406. Further reference cited there, and numerous patents.

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reaction system becomes essentially monovariant and the reaction according to

$$ZnS_{(solid)} + Fe(\gamma) = FeS(\beta) + Zn_{(vap.)} \quad . \quad . \quad (1)$$

will proceed practically to completion at reduced pressure.

If the values for the free energy of formation of the two sulphides (based on thermochemical data and directly measured entropies) adopted by Kelley are combined with the vapour pressure formula of zinc, the free energy of reaction (1) in the relevant temperature range from 900° to 1100° c. is given by

$$\Delta G^\circ = 48{,}500 - 34{\cdot}50T \quad . \quad . \quad . \quad . \quad (a)$$

The thermochemical values are, however, not in very good agreement with the free energy of the formation of zinc sulphide as derived either from measurements of the solubility of zinc sulphide at room temperature, or with the experimental determination of the equilibrium [2] of $ZnS + H_2 = Zn_{(liquid)} + H_2S$. Similar, but minor, deviations are also found for the equilibrium [2] of $FeS(\beta) + H_2 = Fe(\alpha) + H_2$. All these latter investigations tend to suggest a higher value for the free energy of reaction (1), a weighted mean of which would give

$$\Delta G^\circ = 55{,}000 - 34{\cdot}50T \quad . \quad . \quad . \quad (b)$$

In the second column of Table I the temperatures are given at which, according to eqn. (*a*) and (*b*) respectively, the pressure of reaction (1) would equal the values of 1, 10 and 100 mm.

TABLE I

p_{Zn} mm. Hg		t° c	p_{ZnS} mm Hg
1	*a*	740	$3{\cdot}5 \times 10^{-5}$
	b	880	$1{\cdot}4 \times 10^{-3}$
10	*a*	850	$9{\cdot}5 \times 10^{-4}$
	b	1000	$2{\cdot}0 \times 10^{-2}$
100	*a*	1000	$2{\cdot}0 \times 10^{-2}$
	b	1170	$4{\cdot}5 \times 10^{-1}$

In order to obtain some information on the rate of the reaction at the temperatures concerned (below 1000° c.), cylindrical briquettes (1″ diam., weight approximately 30 g.) of a fine powder of zinc sulphide (passing 100 mesh) and either fine or coarse iron powder were pressed, and heated inside the mild steel heating tube of a vacuum induction furnace (residual pressure 0·1 mm.) at temperatures varying from 920° to 1000° c., for times from ½ to 2 hr., the time to reach the temperature being kept constant at 20 min. Two samples of zinc sulphide were used, an ore concentrate containing 79·5 % zinc sulphide and a commercial (synthetic) product containing 97·7 % zinc sulphide. The distilled zinc was condensed on a tagger and weighed. The results with each of the sulphides or iron powders did not differ materially, and showed that conversion could be regarded as complete after 1 to 3 hr., according to the temperature. For instance, in a series of runs carried out at 940° c., 33, 83·5 and 97·3 % of the total available zinc was distilled after 0 (heating period), 2 and 3 hr., and it was further found that the reaction was completed in between 45 and 60 min. at 1000° c.

It was, however, noticed that the loss of weight of the briquette was always greater than the weight of zinc obtained, this being ascribed to evaporation of zinc sulphide and subsequent reaction of the vapour with the iron heating-tube.

The vapour pressure of zinc sulphide in the temperature range between 765° and 1223° c. has been found [3] to be given by $\log p(\text{mm.}) = \frac{-14{,}200}{T} + 9{\cdot}495$.

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[2] References cited by Kelley.[1]

[3] Veselovskii, *J. Appl. Chem., U.S.S.R.*, 1942, **15**, 422. *A.C.S. Abstr.*, 1943, **37**, 3987.

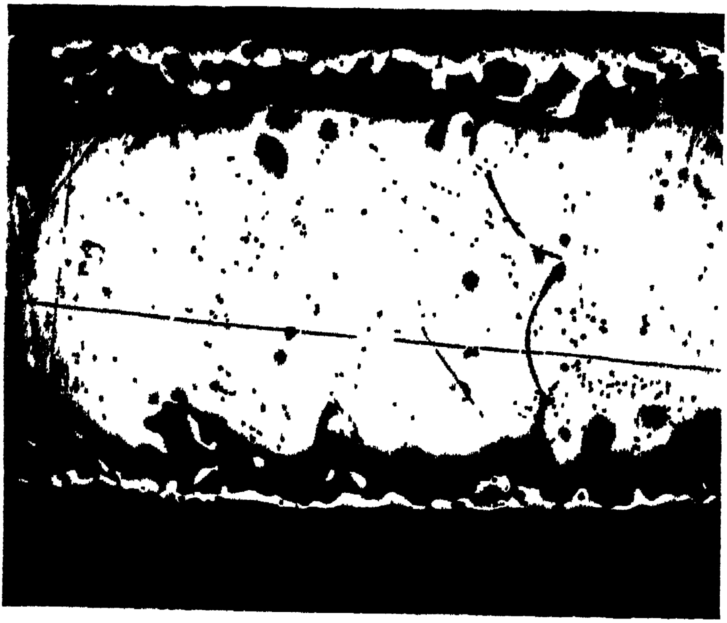

Fig. 1.—Longitudinal section of iron wire, 1 mm. diam., after attack by saturated ZnS vapour for 1 hr. (× 50).

For comparison, the vapour pressure of zinc sulphide is included in Table I (Column 3). Although it is much smaller than the pressure of reaction (1) if either of the eqn. (*a*) or (*b*) is used, appreciable evaporation may occur if the rate of evaporation greatly exceeds the rate of reaction, especially near the end of reaction.

The equilibrium of the exothermic reaction

$$ZnS_{(vap.)} + Fe(\gamma) = FeS(\beta) + Zn_{(vap.)} \quad . \quad . \quad . \quad (2)$$

can be calculated from Veselovskii's equation and either (*a*) or (*b*). The equilibrium constant of (2), $\frac{p_{ZnS}}{p_{Zn}}$, so obtained is $1 \cdot 0 \times 10^{-4}$ (*a*) and $1 \cdot 7 \times 10^{-3}$ (*b*) and $1 \cdot 8 \times 10^{-4}$ (*a*) and $2 \cdot 3 \times 10^{-3}$ (*b*) at 900° and 1000° C. respectively, i.e., effectively total conversion of zinc sulphide vapour into zinc occurs at these temperatures. Because of the solubility of iron sulphide in iron, the conversion will go even nearer to completion than indicated by these figures. Any noticeable contamination of the distillate by zinc sulphide can be avoided by controlling the condenser temperature carefully and filtering the vapour (as suggested for other purposes by Kelley), since the ratio zinc sulphide to zinc at the condensation temperature of zinc is only of the order of 10^{-13} to 10^{-11}, dependent on the evaporation temperature of zinc sulphide (900° and 1000° C. respectively).

In order to obtain qualitative information on the rate of reaction between zinc sulphide vapour and iron, experiments were carried out in which zinc sulphide, contained in a small fireclay boat, was evaporated in the same furnace as previously, the iron heater tube being provided with a silica lining. The zinc sulphide vapour was passed over iron wire or gauze. Keeping the temperature at 1000° C., about 6 g. of zinc were distilled per hour. Only that part of the wire or gauze near the zinc sulphide boat was visibly attacked by the vapour. The rate can be estimated from Fig. 1, which shows the depth (about 0·1 mm.) to which the iron sulphide had penetrated into the iron wire by the reaction.

A typical analysis of the distillate obtained from the ore was Pb 0·11 %, Cd 0·011 %, and the remainder zinc.

Our thanks are due to the Directors of Messrs. High Duty Alloys Ltd., in whose laboratory this work was carried out during 1944, for their interest and for permission to publish these results. We are also grateful to Mr. S. Dilnot for his helpful co-operation.

Summary

Thermodynamic data show that the reaction between $ZnS_{(solid)}$ and $Fe(\gamma)$ at reduced pressure ($p \lesssim 10$ mm. mercury) occurs below 1000° C. Experiments show the rate at this temperature to be sufficient. Thermodynamic data show the ratio of $ZnS_{vap.}$ to $Zn_{vap.}$ in contact with iron at 900°–1000° C. to be very small, and experiments show that the rate of the exothermic reaction between $ZnS_{vap.}$ and $Fe(\gamma)$ is sufficiently high.

Fulmer Research Institute,
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GENERAL DISCUSSION

Dr. F. D. Richardson and Mr. J. H. E. Jeffes (*B.I.S.R.A., London*) (*partly communicated*) : With reference to the paper by Prof. Dannatt and Dr. Ellingham, it is of interest to consider what justification there is for plotting $\Delta G°$ for various reactions against T as straight lines, since neither $\Delta S°$ nor $\Delta H°$ is independent of temperature. Firstly, of course, it is well known that $\Delta S°$ and $\Delta H°$ do not change greatly with temperature except at the phase-change points. Secondly, the changes in both $\Delta H°$ and $\Delta S°$, which arise from variations in the specific heats of reactants and resultants, affect the free-energy changes in such a manner as nearly to compensate. This is illustrated by the following figures for the three most accurately studied of the reactions shown :—

Reaction	Temp. °C.	ΔH°	ΔS°	ΔG°	ΔH°	ΔS°	ΔG°	$\delta(\Delta G^\circ)$
		From full equations			From straight line plots			
$2H_2 + O_2 \rightarrow 2H_2O$	0	− 115·5	− 21·7	− 109·9	− 118·1	− 26·7	− 110·6	+ 0·7
	727	− 118·5	− 26·4	− 92·1	− 118·1	− 26·7	− 91·4	− 0·7
	1727	− 120·7	− 28·1	− 64·5	− 118·1	− 26·7	− 64·5	0·0
$2CO + O_2 \rightarrow 2CO_2$	0	− 135·2	− 41·5	− 123·6	− 135·1	− 41·5	− 123·6	0·0
	727	− 135·1	− 41·7	− 93·4	− 135·1	− 41·5	− 93·6	+ 0·2
	1727	− 132·7	− 40·1	− 52·4	− 135·1	− 41·5	− 52·2	− 0·2
$2C + O_2 \rightarrow 2CO$	0	− 52·9	+ 42·2	− 64·4	− 53·4	+ 41·8	− 65·0	+ 0·6
	727	− 53·4	+ 42·5	− 95·9	− 53·4	+ 41·8	− 95·2	− 0·7
	1727	− 58·5	− 39·0	− 136·5	− 53·4	+ 41·8	− 137·1	+ 0·6

(ΔH° and ΔG° in kcal., ΔS° in cal./degree.)

This shows the values of ΔH°, ΔS° and ΔG° as calculated from the well-established equations which give slightly curved plots and the corresponding values given by straight line plots. It is to be noted that although the straight line plots make it impossible to obtain *accurate* values of ΔS° and ΔH° by means of tangents and intercepts, and give only mean values for each over the range 0° to 2000° C., the errors in ΔG° caused by their use are very small indeed. Except in the cases of these three reactions they are much less than the absolute limits of accuracy of the measurements on which the lines are based. Within these limits, therefore, the free energy equations may be written in the form $\Delta G^\circ = x - Ty$. The complete free-energy equations frequently cited consist of a large number of almost completely compensating terms, which in general go far beyond the probable accuracy of the data used, and are therefore quite unnecessary.

Dr. O. Kubaschewski (*Teddington*) said : I believe that diagrams of the kind shown in the paper by Dannatt and Ellingham give a better representation of free energy values than do formulæ derived without simplification from heats of formation, entropies and heat capacities. Such formulæ may contain up to six terms and are unduly cumbersome. They may also give a false impression of their accuracy, which is seldom within 1000 cal. It is well worth repeating the suggestion that the temperature dependence of free energies should be represented either as in Dr. Ellingham's papers or as simple formulæ of the type $\Delta G_T = \Delta H' + IT$, or involving a constant ΔC_p term, $\Delta G_T = \Delta H' + aT \log T + IT$. This calls for more work on the part of the critical evaluator, but would facilitate the application of the data.

Dannatt and Ellingham's diagrams and data doubtless represent a valuable summary of earlier work on the thermodynamics of metallic compounds. There is only one statement which may be a little misleading and which is of some practical interest nowadays. The free-energy curve given for titanium dioxide is correct so far as we can tell from the basic data. But there are lower oxidation steps of titanium in which the oxygen is bound more strongly, viz., Ti_2O_3 and TiO. Taking this into consideration the ΔG curve for titanium should be placed much lower and far below that of Al_2O_3 in the neighbourhood of that of MgO. Even in the formation of titanium-aluminium alloys the reduction of titanium oxide with aluminium would not lead to alloys containing more than a few % titanium. In practice, and from thermodynamical calculation, the halides of titanium are more likely to be reduced (even by hydrogen) than are the oxides. Work carried out at the National Physical Laboratory shows that there is very little chance of direct reduction of titanium oxides, while experimental measurements of equilibria with the halides and hydrogen indicate a considerable yield of titanium at temperatures of 1100°–1250° C.

Unfortunately the thermochemical values of the metals of the titanium, vanadium and chromium group are rather scarce. Any future thermochemical

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[1] Fink, van Horn and Budge, *Trans. Amer. Inst. Min. Met. Eng.*, 1931, **93**, 421.

measurements on these elements and their compounds will be most useful to metallurgy.

Mr. E. F. Emley * (*Manchester*) (*communicated*): In connection with the free-energy chart for metallic oxides given in Prof. Dannatt and Dr. Ellingham's paper, I would like to ask whether the chart is intended to cover all metals for which information is available, or whether there may be further data available in the case of those alkali and alkaline earth metals which are not included in the chart.

A knowledge of the order of the electropotentials of the alkali and alkaline earth metals in their oxides would be of considerable interest to the magnesium industry. Ruff and Busch [2] infer that the order is the same as that in the fluorides so far as Li, Mg, Ca and Ba are concerned. This would place these elements in descending order of electropotential as follows: Ca, Li, Ba and Mg, an order which does not accord entirely with our own experience. The fluoride electromotive series, based on some magnesium reduction experiments of Busch [2] and our own personal experience, appears to begin (in descending order): Ca, Li, Ba, (Al ?), Mg, Ce, Na, K, Be, thus representing a reversal of the usual order so far as Mg, Na and K are concerned. The order given for the fluorides involves the assumption that the alkali metals are associated in molten magnesium, as was found to be the case in molten tin, antimony and bismuth [3]: otherwise the order would begin Li, Ca, Ba. The order of heat content at room temperature of the fluorides † (ΔH_e^{298}) is Li, (Ca, Sr), Ba, Na, K, (Ce,‡ Mg), Al. Unfortunately, the entropies of most fluorides in the standard states are inadequately known and high-temperature data are incomplete, so that a rough calculation of the free-energy order of the molten fluorides is not easy. If the entropies are estimated by semi-empirical methods,[4] the order obtained is not materially altered.

Comparing this series for heat content with the observed electropotential order given above, it seems possible that since magnesium is "out of step," the entropy of MgF_2 may be considerably greater than would be expected from the semi-empirical estimates. Even with the "expected" figure, however, it appears probable that the free energy–temperature curves for MgF_2 and KF will cross below the melting point of KF.

The position of Al is interesting. Although the reduction of AlF_3 by Mg would be expected, AlF_3 can, nevertheless, be safely employed in fluoride welding fluxes for magnesium alloys,[5] even for alloys in which small amounts of Al are harmful. There is no doubt that the AlF_3 dissolves in the flux, and since the MgF_2 formed by reaction would also dissolve in the flux, there seems no reason why the reaction should "block" on "diffusional" grounds. Is it possible that AlF_3 does not dissociate to an appreciable extent in fluoride melts §; is the entropy of AlF_3 unexpectedly high; or is there some other explanation of the apparent inertness of AlF_3 to magnesium? Compound formation with one of the other fluorides present in the flux (LiF, MgF_2 or SrF_2) might be a possibility, but it may be noted that with even such a well-defined compound as cryolite the NaF is readily reduced by Mg leaving AlF_3, despite the very high heat of

[2] Ruff and Busch, *Z. anorg. Chem.*, 1925, **146**, 87.

[3] Jellinek and Wolff, *Z. anorg. Chem.*, 1925, **146**, 329.

[4] Wenner, *Thermochemical Calculations* (New York, 1941), 176; Treadwell and Mauderli, *Helv. chim. Acta*, 1944, **27**, 567.

[5] *Brit. Pat.* 597,206.

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* Metallurgist, Magnesium Elektron Limited.

† Unless otherwise stated, the figures have been taken from Bichowski and Rossini's *Thermochemistry of Chemical Substances* (New York, 1936). Elements lying particularly close together are shown in brackets.

‡ The heat content of cerium fluoride has been assumed to be the sum of the heat contents of its ions in the aqueous state. This is probably justifiable, as the heat of solution of CeF_3 is unlikely to exceed about 1000 cal.

§ In this connection, it is interesting to note that MgF_2 is apparently undissociated in fluoride melts (Grube, *op. cit.*).

formation of cryolite. Formation of a complex ion, NaF_3^{--}, does however prevent Na being electrolysed before Mg in fluoride melts containing NaF.[6]

It is interesting to compare the electromotive series in the molten chlorides with that in molten fluorides. The order of heat content of the aqueous chlorides at infinite dilution (ΔH_∞^{298}) is Li (Sr, Ca), Ba, K, Na, (Mg, Ce), Be, Al, i.e., the same as that of the aqueous fluorides.* If the heats of solution (Q_S) are added † to the values of ΔH_∞^{298} to give the order of the heat contents of the anhydrous salts, it is found that in the case of the fluorides the only change in the series is to reverse Na and K, thus giving the order quoted above for both the heat contents (ΔH_c^{298}) and the estimated free energies at room temperature of the anhydrous fluorides. Addition of the corresponding heats of solution to the ΔH_∞^{298} values for the chlorides completely alters the order of the elements, because the heats of solution vary considerably both in magnitude and in sign, giving the order (K, Ba), (Sr, Na, Li), Ca, Ce, Mg, (Be, Al). This is in general agreement with that inferred for the molten salts from published data on decomposition potentials and magnesium reduction experiments,[7] namely (Ba, K), (Sr, Li, Na), Ca, (Ce, Mg), Be, Al, although the interpretation of the reduction experiments is complicated by uncertainty as to the state of association of the alkali metals in magnesium.

Except then for the apparent anomalies shown by Mg and Al, the differences between the electromotive series in molten chlorides and fluorides appear attributable as a first approximation to the varying heats of solution of the salts. ‡

If the published values of ΔH_f^{298} are compared with the "calculated" values given by the expression $\Delta H_{\infty(M^+)}^{298} + \Delta H_{\infty(A^-)}^{298} + Q_{s(MA)}$ for the chlorides of Li, Na, K, Ca, Sr, Ba, Mg, Ce, La, Be and Al, the differences amount merely to a few hundred calories in each case, except in that of Ce where the difference is nearly 9000 cal. The value of —252,500 cal. obtained by the above expression accords however with both the published and "calculated" values for $LaCl_3$ (namely, —253,100 and —253,650 respectively). For these reasons, and also from the observed closeness of Ce to Mg in the electromotive series for molten chlorides, it seems very probable that the published figure of —261 500 cal. for ΔH_c^{298} of $CeCl_3$ is incorrect.

A knowledge of the positions of magnesium in the oxide, fluoride and chloride electromotive series is of great practical importance, since these positions govern the practicability of introducing various elements into magnesium alloys and of removing impurities by fluxing methods. By way of example, the introduction of zirconium into magnesium may be considered. As the metal powder is expensive and highly inflammable, it is natural to consider the possibility of alloying by a reducible zirconium compound. The oxide is a refractory substance, and the chloride and its double salts with the alkali metal chlorides are volatile and readily hydrolysed. One is tempted therefore to try the fluoride. This is a solid substance, though somewhat volatile, and with it zirconium can be introduced under certain conditions by prolonged stirring at 920°–950° c. To enable the reaction to proceed readily at reasonable temperatures, some solvent for the ZrF_4 is clearly required. If KF, forming the double salt K_2ZrF_6 melting about 840° c., is used, the magnesium will reduce the KF explosively. The use of LiF, though quite safe, is of course impracticable for economic reasons.

We have made the curious discovery that any chloride will apparently suppress the violent reaction of KF with magnesium, and I wonder if anyone can tell us why this should be so. The effect is evidently not one of dilution, since equal

[6] Grube, *Z. Elektrochem.*, 1927, **33**, 481.

[7] Grambi and Devoto, *Gaz. chim. ital.*, 1927, **57**, 836; Jellinek and Czerinuski, *Z. physik. Chem.*, 1924, **110**, 192; *Z. anorg. Chem.*, 1924, **139**, 233.

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* Where "insoluble" substances are concerned, the sum of the heat contents of the component ions at infinite dilution has been taken.

† Subtracting the increase in heat content on solution ($-Q_s$) is equivalent to adding the heat of solution.

‡ The prediction that differences would arise between the fluoride and chloride electropotential series because of the varying heats of solution of the chlorides was made by Jessup in 1919.

dilution with LiF will not prevent violent reaction. Neither is it due to interchange of radicals, since KCl itself will work. X-ray examination of a fused melt of KCl and KF failed to show any lines other than those of these substances, so that compound formation appears to be ruled out. In the presence of KCl, very little reduction of the KF by the magnesium occurs, but the resulting alloy may contain sufficient potassium, though less than 0·001 %, to render it unsuitable for certain purposes. If $BaCl_2$ is substituted for KCl, the KF will react with the $BaCl_2$ to give some BaF_2 which will be appreciably reduced by magnesium, and the resulting alloy containing up to 0·07 % Ba will be unsuitable for sand casting. The alternative use of NaCl has similar disadvantages. If $MgCl_2$ is substituted for KCl on the grounds that it should remove the traces of potassium or barium mentioned above, it is found that the $MgCl_2$ reacts violently with the ZrF_4 to give $ZrCl_4$ which is rapidly lost by volatilisation!

I hope that this indication of the type of problem with which the magnesium industry deals will show the need for an accurate knowledge of the order of electropotential of the alkali and alkaline earth metals in their reducible salts. What are clearly needed are diagrams for chlorides and fluorides similar to the excellent one given by Prof. Dannatt and Dr. Ellingham, and in this connection I would like to echo the opinion expressed by several speakers that a diagram giving the free energy ($RT\ln p$) plotted against temperature is the most practically convenient way of representing free-energy data. I do hope that someone may feel encouraged to undertake this work, and in particular the determination of the entropies of the fluorides. These are imperfectly known, and the need for this information was mentioned to me after the Discussion by two members working in different fields.

One feature of the Debye-Hückel theory of strong electrolytes is, I believe, that it enables activity coefficients to be calculated approximately in terms of the dielectric constant of the solvent and the ionic strength. Perhaps Dr. Richardson or Dr. Bockris would indicate whether work has been done to compare the observed activity coefficients in slags with those calculated from various "models," and if not, whether such work might perhaps give useful information on the average distribution of ionic charges in slags.

Dr. J. O'M. Bockris (*London*) (*communicated*): It has been shown[8] by application of a similar treatment to Debye and Hückel's for dilute solutions of aqueous electrolytes to a dilute solution of one molten salt in another that such systems are ideal at limiting concentrations. Calculations concerning interionic attractions in systems of ionic melts would be particularly complicated because (i) the dielectric constant (the published values of which are rather doubtful) are probably low compared with that of water; (ii) the ions are much closer together than in aqueous solutions. Both these, and other, effects render some approximations made in the theory of interionic attractions for dilute aqueous solutions quite inapplicable to ionic melts and the resulting mathematical difficulties are very considerable. Ion-ion induction and dispersion forces would be much more important in liquid salt systems, too, though negligible in dilute aqueous solution. An intrinsic difficulty concerning the reference state for individual ionic activities in liquid salts has been discussed by Temkin.[9]

Dr. F. C. Frary (*New Kensington, Pa.*) said: Dannatt and Ellingham repeat the usual equation for the net result of the electrolysis of Al_2O_3, showing the production of CO at the anode. Analysis of the anode gas, however, shows it generally to contain at least 60 % of CO_2. Taking into consideration the very considerable opportunity which the gas has had for contact with incandescent carbon floating on the molten cryolite bath, and with the anodes themselves, it would appear that the gas as produced must have been mostly CO_2, and the reaction on which the decomposition voltage is calculated should be

$$2Al_2O_3 + 3C = 4Al + 3CO_2.$$

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[8] Gross, *Z. anorg. Chem.*, 1926, **150**, 339.

[9] Temkin, *Acta Physicochim.*, 1945, **20**, 411.

Mr. J. A. S. Mowat (*Cambridge*) said: Plotnikov and Razumov [10] report that it is possible to reduce oxides of iron with hydrogen and CO at room temperature in the presence of a high-frequency electromagnetic field.

Dr. Herasymenko has kindly translated the paper for me, and the main points are—

(i) The reduction of Fe_2O_3 takes place in two stages:

(*a*) Fe_2O_3 is reduced to Fe_3O_4;

(*b*) Fe_3O_4 is reduced to metallic iron ($Fe(OH)_3$ is reduced more readily than Fe_2O_3).

(ii) The maximum yield of metallic iron is 21 % from pure Fe_2O_3, but only 5 % from iron ore.

(iii) The reaction begins at room temperature, without heating; the temperature rises to 60°–80° C. because the reaction is exothermic.

(iv) Carbon monoxide alone will not react with iron oxides, but mixtures of CO and H_2 will reduce the oxide, and CO_2 is detected in the resulting gas mixture.

I understand that the reactions are thermodynamically possible, but would like to know why the alternating electromagnetic field should assist the reaction, and whether other metallic oxides might be reduced in the same way.

Dr. H. J. T. Ellingham (*London*) (*partly communicated*): The information furnished by Dr. Kubaschewski on lower oxides of titanium is of great interest. It is recognised, moreover, that there may be other cases where lower oxides which are more stable over at least part of the temperature range (Dr. Welch has referred to SiO) may make the effective affinity of the element for oxygen different from that represented by the line for the oxide in the $(-\Delta G) - T$ diagram in our paper. Data for all the oxides of the various elements are required in order to obtain a complete picture of the scope of possible oxidation and reduction processes. In reply to Mr. Emley's question it should be stated that data for certain oxides not represented in the above-mentioned diagram are available, though in many instances they are less accurate than those for the oxides shown. For oxides of the alkali and alkaline earth metals, other than sodium, calcium and magnesium, the figures are scanty and of doubtful reliability, especially at higher temperatures, and further experimental work in this field is certainly needed.

Mr. Emley's plea for the provision of similar $(-\Delta G) - T$ diagrams for chlorides and fluorides should be strongly supported and, in view of the importance of such diagrams in the elucidation of processes for the production of the light metals and their alloys, it might be expected that the research establishments of the industries concerned would undertake, or at least sponsor, the necessary free-energy determinations. For this purpose the electrochemical methods illustrated in the paper by Rose, Davis and Ellingham [11] may be largely applicable; they have the advantage of yielding directly the required free-energy data over ranges of temperature in which the measurements can be made. Thus, for chlorides, determinations of the E.M.F. of cells of the type $M|MCl_x|Cl_2$ can be readily made, while for chlorides and fluorides measurements of decomposition voltage might be useful. Moreover, such methods lend themselves to the determination of the free energy of formation of substances in mixed melts and can thus serve for the direct investigation of such problems as have been mentioned by Mr. Emley in connection with the relative affinities of magnesium and related metals in halide systems where complex formation is likely to affect the normal sequence. It may well be, as Mr. Emley indicates, that in single salt melts the sequence of the elements in respect of free energy of formation of chlorides may differ from that of fluorides and that the latter may be more akin to that of oxides. It is clearly important to secure more data in this field.

On the point raised by Dr. Frary, the reference in our paper to the minimum voltage required for the electrolysis of a melt saturated with alumina, using a carbon anode, relates to the production of the $CO - CO_2$ mixture in equilibrium with carbon at the specified temperature, and at practical operating temperatures this corresponds to a notable preponderance of CO. At the high current densities employed in practice, however, the proportion of CO_2 will tend to be higher than that represented by equilibrium and the gas evolved at the anode may well be largely CO_2. If the equation

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[10] *Acad. Sci., Ukrainian U.S.S.R.*, 1936, **3** (2), 153.

[11] This Discussion.

$$2Al_2O_3 + 3C = 4Al + 3CO_2$$

were taken as the basis of reference, the " minimum " voltage would be given at any temperature by the distance between the lines for formation of Al_2O_3 and of CO_2, instead of between those of Al_2O_3 and the equilibrium $CO - CO_2$ mixture, and would therefore be somewhat higher (about 0·1 v. at 900° c.), but it is held that this would be a somewhat artificial basis to adopt. In any event, polarisation and resistance factors combine to make working voltages much higher than the minimum, which corresponds to the ideal condition of zero current density.

The reference to reduction of oxides of iron with hydrogen and CO in a high-frequency electromagnetic field, brought forward by Mr. Mowat, is of interest. It seems probable that the effect of the alternating field in assisting the reaction may be due to local heating effects.

Sir Charles Goodeve (*B.I.S.R.A., London*) said : Anyone coming into this field is faced, sooner or later, with a decision between two methods of plotting equilibrium pressures or constants, the " log p against $1/T$ " method used by Pourbaix and Rorive-Bouté, and the " $RT \log p$ against T " method as used by Dannatt and Ellingham. Each of these has its advantages and disadvantages. They both give plots which are very close to straight lines, thus permitting ready interpolation or extrapolation and from slopes or intercepts mean values of ΔH and ΔS can be derived. It is somewhat easier to visualise a vapour pressure than a chemical potential or free energy, but against this, the $1/T$ scale is awkward. In every other direction, the second method scores. It is the natural method to follow the thermodynamic calculations by which most of the data are derived from observations or theory. It permits a wide range of data to be plotted on one diagram and at the same time gives a uniform openness of the scale for each range of temperature. This arises from the fact that, for a series of reactions of a given type, the entropy change is much the same for each, whereas the heat content change may vary over a very wide range ; this could be seen if an attempt were made to plot the information given in Dannatt and Ellingham's Fig. 1 and 2 on a $\log p - 1/T$ basis. Indeed, the free energy or chemical potential basis brings out in a striking manner the variation in entropy changes which play such an important part in the development of our knowledge of the various states of matter.

The curves of Pourbaix and Rorive-Bouté bring out in a beautiful way the equilibria over a range of conditions of practical importance to those dealing with metals. I would like to suggest, however, that they try replotting some of these on the chemical potential basis which is now widely accepted as standard. This would have the advantage of strengthening the standard and would be unlikely to be less effective in bringing out the points in their paper.

Dr. M. J. N. Pourbaix and Madame C. Rorive-Bouté (*Brussels*) (*partly communicated*) : As mentioned by Sir Charles Goodeve in his paper, the partial pressure of zinc oxide vapour over solid zinc oxide is very low, even at 1200° c. The values given for its vapour pressure in the literature, especially those of Feiser, seem to be incorrect, in the sense that solid ZnO probably does not *sublime*, but *decomposes* into oxygen and gaseous zinc according to the reaction,

$$2ZnO\ (\text{solid}) = 2Zn\ (\text{gas}) + O_2.$$

The influence of the temperature on the equilibrium constant of this reaction, and on the decomposition pressure ($P = p_{Zn} + p_{O_2}$) of ZnO may be expressed approximately by the two relations,

$$\log (p_{O_2} . p^2_{Zn}) = -48{,}520/T + 20{\cdot}90,$$

and

$$\log_{10} P = -16{,}173/T + 7{\cdot}24.$$

The equilibrium conditions for the reduction of ZnO by CO according to the reaction,

$$ZnO\ (\text{solid}) + CO = Zn\ (\text{gas}) + CO_2$$

under atmospheric pressure, may be easily known if we draw on the equilibrium diagram of the system Zn — C — O (Fig 3 in our paper, this Discussion, or Fig 3 here), the line relating to the two conditions

$$p_{Zn} = p_{CO_2}$$

and

$$p_{CO} + p_{CO_2} + p_{Zn} = 1 \text{ atm}$$

Such a line has been drawn in Fig 3 here for which according to the excellent

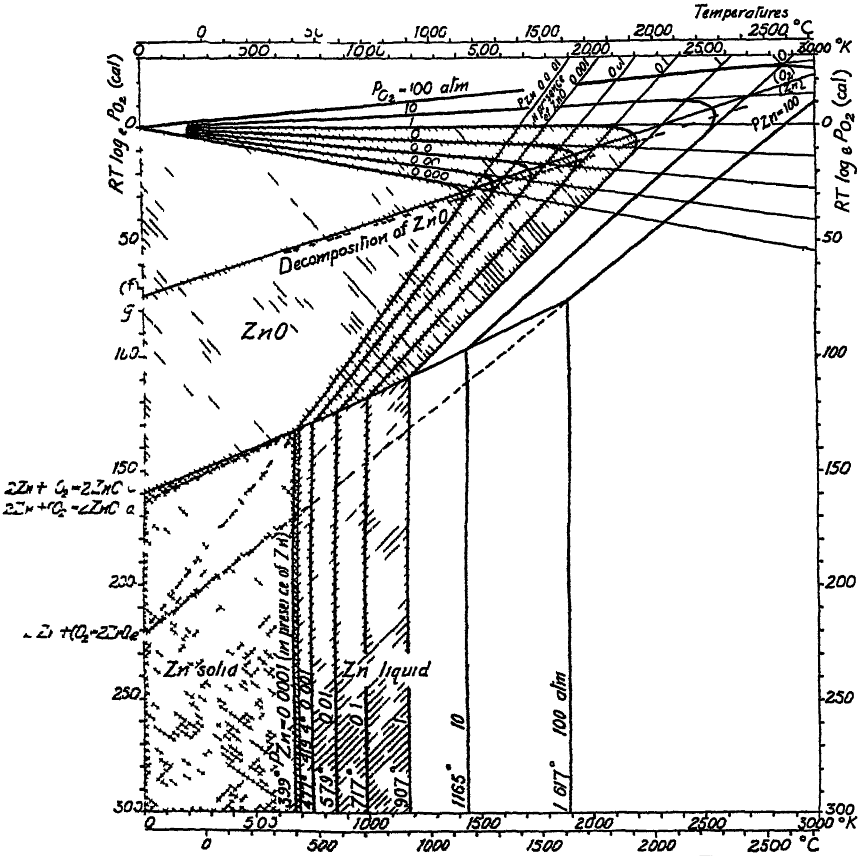

FIG 1 —Equilibrium zinc-oxygen

suggestion made by Sir Charles Goodeve, we have adopted $RT \log_e p_{O_2}$ and T as independent variables This line leads to the values for the influence of the temperature on the composition of the gaseous phase (Table I)

TABLE I

T (°K)	t (°C)	% CO	% CO_2	% Zn
1216	943	80	10	10
1340	1067	60	20	20
1448	1175	40	30	30
1580	1307	20	40	40
1690	1417	10	45	45

It is noticeable that this line intersects the 1 atm.-isobar at a point the abscissa of which is $T = 1130°$ K. (857° C.). This signifies that, below this temperature, solid carbon may be formed as a stable phase according to the reaction

$$2CO \text{ (gas)} = C \text{ (solid)} + CO_2 \text{ (gas)}.$$

It is thus probable that, below 857° C., ZnO may catalyse the decomposition of CO according to this reaction.

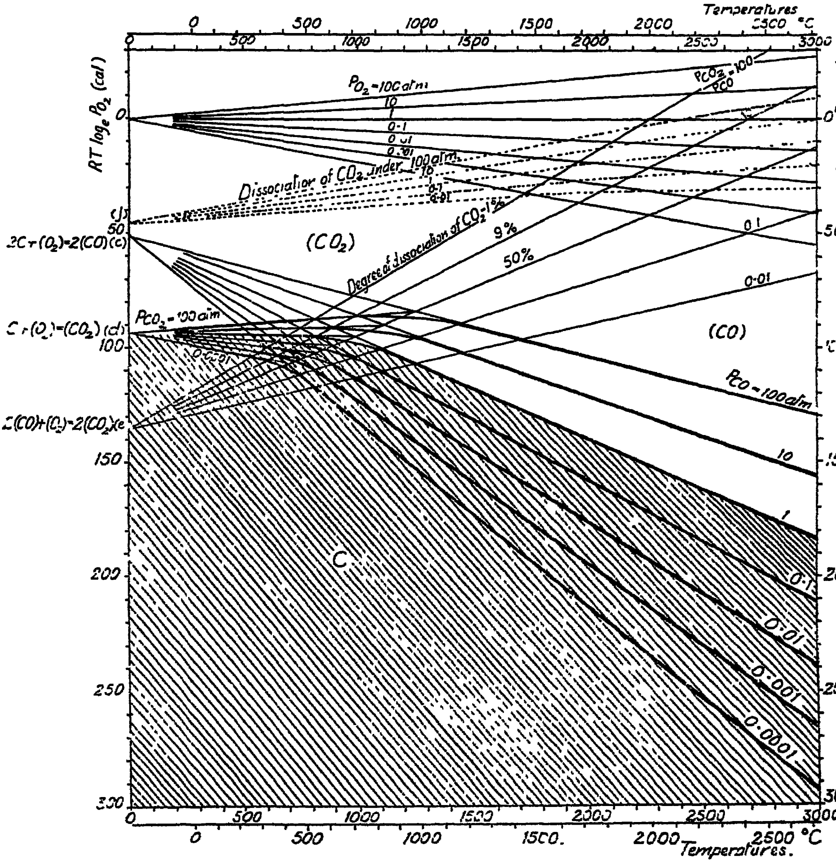

FIG. 2.—Equilibrium carbon-oxygen.

Sir Charles Goodeve has suggested that our graphical method for the study of complex oxidation equilibria would be advantageously modified by plotting $RT \log_e p_{O_2}$ as a function of T, instead of $\log p_{O_2}$ as a function of $1/T$. In accordance with this valuable suggestion we have re-drawn the three equilibrium diagrams for the systems Zn–O, C–O and Zn–C–O presented in our paper (Fig. 1, 2 and 3 here). We quite agree that this modified representation is, in most cases, better than the previous one. The isobars are somewhat more difficult to draw, and it is not possible to give in a small space an overall picture of everything that may happen between ordinary and very high temperatures. On the other hand, the use of a linear scale for temperature makes these diagrams more easy to utilise, and, as pointed out by Sir Charles Goodeve, the precision is better for the higher temperatures, which are usually of particular interest.

A comparison of this method with our previous one and with the original method of Ellingham leads to the following statement —

The free energy of a given oxidation reaction, per gram molecule of oxygen, may be expressed as follows—

$$-\Delta G = RT \log_e p_{O_2} + RT\,\Sigma\,\nu \log_e p_B = -\Delta H + T\Delta S$$

where p_B represents the partial pressures of the reacting gases other than O_2

(i) In our original method (Fig 1, 2 and 3 of our paper), the equilibrium oxygen pressure of every possible reaction has been plotted as a function of $1/T$ according to the relation

$$\log_{10} p_{O_2} = -\frac{\Delta H}{2\cdot 3\,RT} - \frac{\Delta S}{2\cdot 3\,R} - \Sigma\,\nu \log_{10} p_B \qquad (1)$$

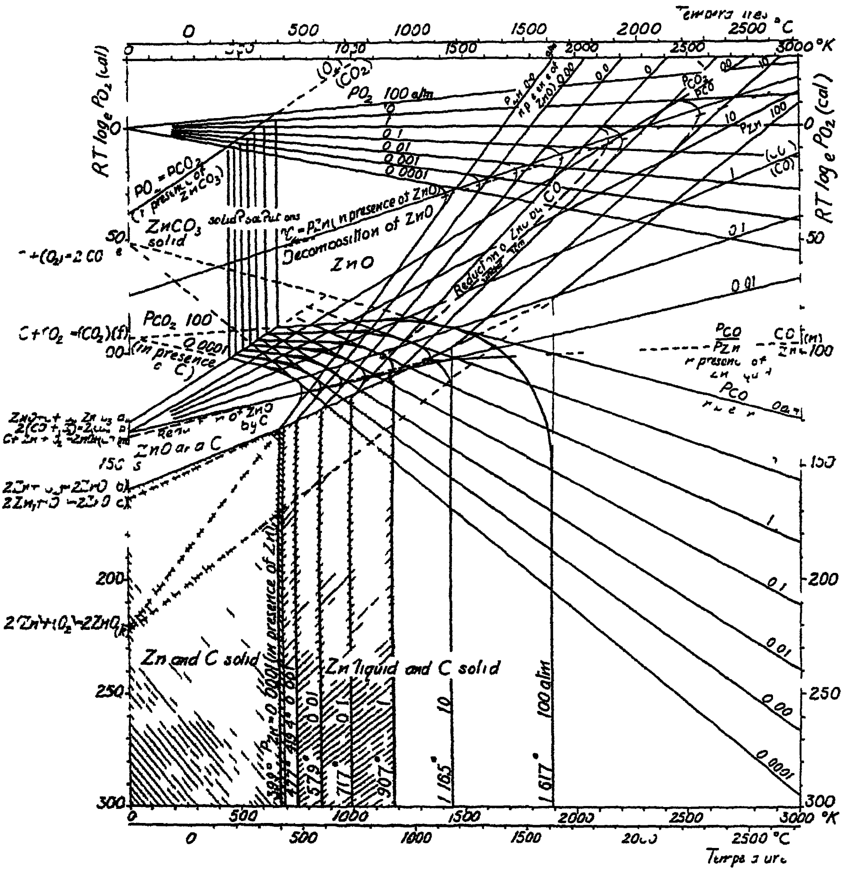

FIG 3 —Equilibrium zinc-carbon oxygen

The equilibrium of every reaction is thus represented by a line, or by a group of parallel lines, each of which relates to a given value of the parameter $\Sigma\,\nu \log_{10} p_B$ The slope of the lines measures the heat content change, ΔH, of the reaction, lines relating to exothermic oxidation reactions rise from left to right, the lines relating to endothermic reactions fall from left to right The intercepts of those lines with the y-axis, the parameter of which is equal to zero, measures the entropy change of the reactions

(ii) In the modified method (Fig 1, 2, 3 here) suggested by Sir Charles Goodeve, $RT \log_e p_{O_2}$ is plotted as a function of T, according to the relation

$$RT \log_e p_{O_2} = -\Delta H + T\Delta S - 2\cdot 3\,RT\,\Sigma\,\nu \log_{10} p_B \,. \qquad (2)$$

The equilibrium conditions of every reaction are thus represented by a line, or by a group of lines, each of which relates to a given value of the parameter $\Sigma \nu \log_{10} p_B$. For a given temperature, the tangents to all lines of a given group meet at a single point, situated on the y-axis, the ordinate of which measures, as pointed out by Ellingham, the heat content change ΔH of the reaction; for exothermic oxidation reactions, the ordinate of this concurrence point is negative; for endothermic oxidation reactions, it is positive. The slope of those lines, the parameter of which is equal to zero, measures the entropy change ΔS of the reaction.

(iii) In Ellingham's original method, $-\Delta G$ is plotted against T according to the relation

$$-\Delta G = -\Delta H + T\Delta S \quad . \quad . \quad . \quad . \quad (3)$$

and a "pressure correction chart" is given, which represents, for different pressures, the influence of the temperature on the value of the function $RT \log_e p$. If, as has since been done by Ellingham[12] one draws on the same diagram, for a given reaction, the lines corresponding to relation (3) with the pressure corrections for all gaseous components B other than O_2, one obtains a group of lines the equation of which is

$$RT \log_e p_{O_2} = -\Delta H + T\Delta S - 2{\cdot}3\, RT\, \Sigma \nu \log_{10} p_B$$

identical with relation (2).

By drawing on the same diagram such lines and groups of lines for every reaction of practical interest which may occur in a given system, and by completing this diagram with isobar lines, one obtains a figure which is exactly the same as figures of type 2.

It may thus be said that the suggestion made by Sir Charles Goodeve leads to a method of representing complex equilibria, which, by combining particular features of both Ellingham's and Pourbaix's methods, may be of special interest

Dr. H. J. T. Ellingham (*London*) (*communicated*): The comparison made by Dr. Pourbaix of the distinct methods employed by him and by myself for representing thermodynamic data for the formation of oxides, etc., in relation to temperature, is of considerable interest and I welcome his acceptance of Sir Charles Goodeve's suggestion that plotting $RT \log_e p_{O_2}$ against T is, on the whole, to be preferred for practical purposes. As is implied in Pourbaix's discussion, this method is basically the same as my own in which $-\Delta G$ (or E) is plotted on T, and one of its principal advantages lies in the fact that the dependence on temperature of the "driving force" of reactions, whether expressed as a free energy ($-\Delta G$), as an electromotive force (E) or as a function of a partial pressure of oxygen (p_{O_2}), is made directly obvious.

It may be desirable, however, to indicate rather more precisely the significance of the pressure, p_{O_2}, in relation to the free energy of the reaction. In the $(-\Delta G) - T$ diagrams for oxide formation in my own papers[13] the fundamental line for a particular reaction refers to the *standard* free energy, $-\Delta G°$, and thus represents at any temperature the driving force of the process when all of the participating substances (including oxygen) are at unit activity (1 atm. partial pressure for gases that can be regarded as ideal). But, as at any given temperature $-\Delta G°$ is also equal to $RT \log_e K$, where K is the equilibrium constant of the reaction at that temperature, we can write for a reaction of the type, $2M + O_2 = 2MO$:

$$-\Delta G° = RT \log_e \{MO\}_e^2/\{M\}_e^2 \{O_2\}_e$$

where $\{X\}_e$ represents the activity (partial pressure) of X in any condition of equilibrium at the given temperature. For the particular case of an equilibrium in which $\{MO\}_e = \{M\}_e = 1$, i.e., participants other than oxygen at unit activity,

$$-\Delta G° = -RT \log_e \{O_2\}_e = -RT \log_e (p_{O_2})_e.$$

The fundamental lines on such a diagram also represent, therefore, the variation with temperature of the quantity $RT \log_e p_{O_2}$, where p_{O_2} has this special significance, which is in fact the "oxygen dissociation pressure" of the oxide at any specified temperature.

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[12] *XIth Int. Congr. Pure Appl. Chem.* (London, 1947) (in press).

[13] *J. Soc. Chem. Ind.*, 1944, **63**, 125; Dannatt and Ellingham, This Discussion.

If for the formation of a given oxide additional lines be added to the diagram to represent $-\Delta G$ when a participant other than oxygen, say, the element M, is at an activity different from unity, then at any temperature $-\Delta G$ will differ from $-\Delta G^\circ$ by the quantity $2RT \log_e \{M\}$, which for a gaseous substance can be read directly from a correction chart showing values of $RT \log_e x$ for various values of x. Moreover, if the $-\Delta G$ scale is written as $RT \log_e p_{O_2}$, the significance of p_{O_2} at any temperature is now the partial pressure of oxygen in an equilibrium state in which the activity of the element is $\{M\}$ but that of the other participant is unity. In so far as this is the significance to be attached to p_{O_2}, plotting $RT \log_e p_{O_2}$ against T is the same thing as plotting $-\Delta G$ against T.

Finally, it may be noted that, in as much as both $-\Delta H$ and ΔS for a reaction may vary appreciably with temperature, even over a range within which none of the participants undergoes a change of physical state, strictly straight lines will not be obtained either by plotting $\log_e p_{O_2}$ against $1/T$, or by plotting $-\Delta G$ (or $RT \log_e p_{O_2}$) on T. In either case, therefore, evaluation of heats of reaction and entropy changes from the slopes and intercepts of such lines, as described by Pourbaix, should properly be in respect of the tangent to a line at a particular temperature, though such lines are commonly sensibly straight over a notable temperature range for reasons pointed out by Richardson and Jeffes in this Discussion.

Dr. S. E. Woods (*Avonmouth*) said : Roasting and reduction processes are often very rapid under conditions of practical metallurgical interest and this feature of great rapidity may lead to difficulties of interpretation either (*a*) as to the energy levels involved, if the reaction is strongly endothermic, or (*b*) as to the location of the reaction in cases where two solid phases are involved. The " proof " that in such cases reaction must take place at the solid-solid interface will be familiar from a number of standard texts. The reaction mechanisms proposed by Anderson help to clarify both these points.

The reduction of zinc oxide by carbon monoxide is a case in which the first type of difficulty arises. If we examine the data of Truesdale and Waring,[11] taking for example their result for reduction at 1000° c., and compare the reaction rate per unit area of briquette surface with the calculated collision rate per unit area, we find that a fraction 3×10^{-6} of the collisions resulted in reaction. Their observed rate requires correction in two respects, however, in order to arrive at an estimate of the true kinetic rate per unit area of zinc oxide crystal surface.

(1) Since the rate was controlled by diffusion through an exterior gas film,[15] the gas in contact with the surface must have approached equilibrium concentrations. The rate uncomplicated by back reaction would be more rapid than that measured.

2) With briquetted material the area of surface taking part in the reaction may exceed considerably the exterior surface area of the briquette, so that one's estimate of the rate per unit area of zinc oxide is diminished.

From a detailed consideration of these points the writer believes that the true collision efficiency is unlikely to be less than 1×10^{-5}. From this efficiency one can make maximal estimates of the activation energy of the rate process. Assuming that the whole of this activation energy had to be provided as translational energy of the carbon monoxide molecule, the maximum value would be 35 kcal. If the energy could be provided jointly as translational energy of the gas molecule together with three vibrational degrees of freedom of the solid atom the corresponding figure would be 50 kcal. Both of these figures would be considerably reduced if one makes reasonable allowance for the orientation requirements of a successful collision.

These figures have to be compared with a total endothermic heat of reaction at 1000° c. of about 43 kcal. It seems to the writer that in order to avoid straining probabilities it is necessary to assume that the decisive step of the reaction proceeds to an end state of appreciably lower energy content than the state of completed reaction with both zinc and carbon dioxide in the gaseous state. This would follow naturally from the scheme outlined by Anderson in which removal of oxygen from the lattice is a process more or less distinct from a later evaporation of zinc from the surface. This evaporation should be markedly endothermic, so that the overall heat requirement of the process is subdivided in such a way that the energy of activation can be less than the total endothermic energy change. The rate of reaction would be equal both to

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[11] Truesdale and Waring, *Trans. Amer. Inst. Min. Met. Eng.*, 1944, **159**, 97.

[15] Woods (in press).

(*a*) a rate of oxygen removal given by

$$(\text{Collision rate}) \times (\text{probability factor}) \times e^{-Q_1/RT}$$

and to

(*b*) a rate of zinc evaporation given by

$$(\text{Number of surface zinc atoms/unit area}) \times (\text{vibration frequency}) \times e^{-Q_2/RT}.$$

Then $Q_1 + Q_2$ must equal or exceed 43 kcal., while Q_1 could be considerably less than this value.

With regard to the second difficulty, the classical argument in relation to the reaction

$$A_{\text{solid}} + B_{\text{gas}} \rightleftharpoons C_{\text{solid}} + D_{\text{gas}}$$

is that if the reaction from left to right proceeds at all parts of the surface of A, we should have a rate expression of the form,

$$(\text{Pressure of B}) \times (\text{Surface Area of A}).$$

Considering an equilibrated system and equating two such rate expressions, we arrive at the absurd conclusion that the equilibrium constant depends upon the relative surface areas of the two solids. One is forced to conclude that the reaction occurs at some location which is common for both forward and backward processes; this location is then identified with the solid–solid–gas interface.

It is hardly credible, however, that such reactions, which are often extremely rapid, should be confined to this interface. One way out of the difficulty is to invoke solid solution; diffusion through the crystal lattice of components with minute concentration gradients as driving force would however be a relatively slow process.

The mechanisms advanced by Anderson allow one to treat this question in a simple manner. The composition of the surface is variable to a much greater extent than that of the interior of the crystal, and is sensitive to the nature of the gas in contact with it. Equalisation of forward and backward rates could therefore occur on the surface of a single phase; for example, at the surface of an oxide in contact with the appropriate equilibrium mixture of carbon monoxide and carbon dioxide, the surface composition would adjust itself so that the rate of oxygen removal by carbon monoxide was balanced by the rate of oxidation of surface metal atoms by carbon dioxide. Clearly, the relative amounts of different phases present at equilibrium becomes irrelevant. On the other hand, the diffusion involved is principally a surface migration, which is much more consistent with a rapid overall rate of the process.

Dr. F. D. Richardson and Mrs. E. Dancy (*B.I.S.R.A., London*) (*partly communicated*): Investigations now being made by one of us (E.D.) on the reduction of iron oxide by hydrogen are of interest in connection with Dr. Anderson's paper on primary reactions in reduction processes. Our procedure is to build up layers of wüstite on pure iron strips at 900° c. in a controlled H_2O–H_2 atmosphere, and then to follow their reduction in flowing hydrogen at temperatures from 570° to 900° c. The thickness of these layers is about 100,000 lattice spacings, and the *overall* reduction process shows a temperature coefficient corresponding to a low activation energy of about 7 kcal. The main point of interest is that massive iron is not formed on the surface as reduction proceeds, but that the surface continues to consist of iron oxide for over half the total period of reduction. The test we have applied for detecting the iron is to immerse the strips in dilute copper sulphate solution and then inspect under the microscope for deposited copper. The results suggest that following the removal of oxygen from the surface by the hydrogen gas, the excess iron atoms migrate through the wüstite lattice and deposit on the central massive iron before they can nucleate to form a separate phase elsewhere.

We believe that this does not happen in the reduction of copper oxide which soon produces free copper at the surface, presumably because copper oxide has too few vacant cation lattice sites to permit rapid movement of the copper atoms. In the case of iron oxide, however, the crystal has about 5 % vacant cation sites even when in equilibrium with solid iron. It would seem therefore that during reduction a concentration gradient of vacant lattice sites is built up across the oxide layer, the values being low at the surface being reduced, and 5 % at the iron interface. A steady movement of iron atoms may then take place up this gradient towards the iron, and this appears to be rapid enough to prevent the excess iron nucleating to form a separate phase at the surface. The result is not directly applicable to the reduction of ores in which massive iron does not already exist, but it does give interesting information on the mechanism whereby nuclei may grow once they have formed under normal conditions.

Dr. T. P. Hoar (*Cambridge*) said : Richardson's results for the reduction of oxide films on iron by hydrogen may be visualised in terms of the mechanism for the corresponding oxidations given by Wagner,[16] for which Price and I [17] proposed a simplified model. For the oxidation of iron (Fig. 1) we may consider the oxygen-film-metal system as a current-producing cell, in which the film surface is regarded as an inert basis at which O_2 molecules are cathodically reduced to O^{--} by electrons arriving from the metal through the semi-conducting film, and the metal-film interface is the anode at which metallic iron passes into the film as ferrous ions ; electrolytic migration of these ions through the film, possible because of the vacant sites on the cation lattice, leads to growth of the film,

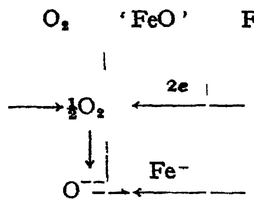

FIG. 1.

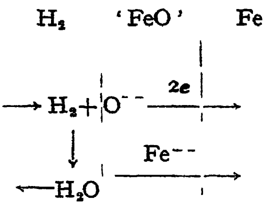

FIG. 2.

which is thus regarded both as metallic connection and electrolyte of the cell, the E.M.F. being equivalent to ΔG (formation) for the oxide. For the reduction (Fig. 2), hydrogen gas and oxide ions react anodically at the film surface, giving H_2O molecules that desorb and electrons that pass through the film to reduce ferrous ions to metal at the now cathodic metal-film interface ; electrolytic migration of Fe^{++} inwards accompanies the process. Anion migration, possible in principle, is likely to be vanishingly small by comparison with cation, because of the larger size of the anions and their complete lattice.

The formation of surface islands of metal, found by Richardson in the case of copper oxide films, indicates the formation of new metallic nuclei in this case : which spatial form the reduction takes must depend on the relative rates of O^{--} removal, cation migration and metal nucleus formation in each case.

In the interpretation of his very interesting results, I think Anderson attaches rather too much significance to the so-called Tammann temperature $(0{\cdot}5T_m)°$ K., where $T_m°$ K. is the melting point. There is much evidence that bulk diffusion in solids can often take place at sensible speeds at much lower temperatures ; for instance, the sulphide films on copper exposed to ammonium polysulphide can grow to several thousand A. in a few seconds at room temperature, and the rate of solid diffusion in the development of the photographic latent image is of a similar order to magnitude.

Dr. J. S. Anderson (*Harwell*) said : Tammann's generalisation, that diffusion processes become significant in solids at temperatures above 0·5 × absolute melting point, is admittedly only a rough rule, and is not meant to be regarded as anything more than that. At the same time, the gross exceptions to the rule fall largely into two special categories : (*a*) structures in which cations are distributed over a larger number of cation sites, so that the distinction between "correctly" and "interstitially" sited cations, or between occupied and vacant sites, loses its usual meaning (examples are α–Ag_2S, AgI, etc.) ; (*b*) structures with an unusually high concentration of interstitial atoms or vacant sites available for participation in the diffusion process. This is true, e.g., for markedly non-stoichiometric phases.

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[16] Wagner, *Z. physik. Chem. B*, 1933, **21**, 25.
[17] Hoar and Price, *Trans. Faraday Soc.*, 1938, **34**, 867.

For the cases referred to in my paper, the use of Tammann's rule is probably valid, for there is a wealth of data extant on the phenomena associated with combination reactions between oxides (e.g., the work of Hüttig's and Fricke's schools), which reveals the onset of surface- and bulk-phase processes successively as the temperature is raised.

Prof. M. Wiberg (*Stockholm, Sweden*) said : In his interesting paper Dr. Woods has pointed out that the reduction of magnetite is not only a simple diffusion-controlled reaction but also controlled by processes within the individual particles.

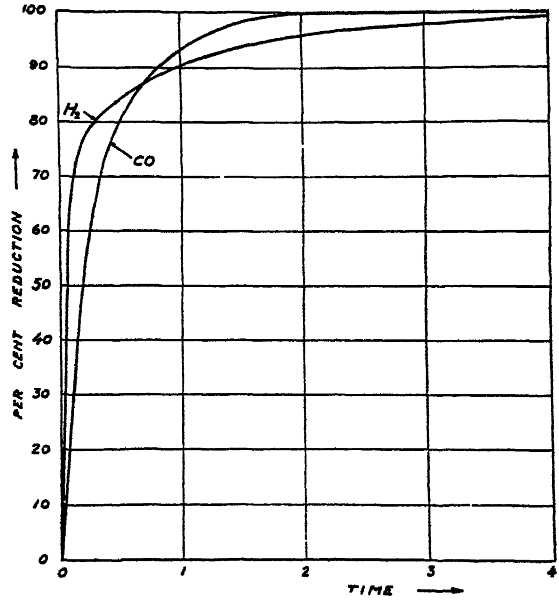

FIG. 1.—Reduction of 2 mm. magnetite grains at 1000° c.

In connection with my efforts to reduce iron ore to sponge iron on an industrial scale I have made some investigations of the reduction of magnetite with carbon monoxide and hydrogen which are in good agreement with Dr. Wood's indication. In one of those investigations 2 mm. grains of a very pure Swedish magnetite from Kiruna were reduced at 1000° c. (Fig. 1). During the first stages of the reduction, when the diffusion seems to be the rate-controlling factor, the hydrogen reduced much faster than the carbon monoxide, but during the final stages the carbon monoxide reduced faster than the hydrogen so that the time for complete reduction was longer with hydrogen than with carbon monoxide. This indicates that something else than diffusion is the rate-controlling factor during the final stages.

Fig. 2 and 3 are microphotographs of the reduced magnetite after 30 min. reduction with carbon monoxide and hydrogen. The black areas are pores, the grey areas wüstite and the white areas are porous metallic iron, surrounding the wüstite particles. The metallic iron seems to be somewhat coarser, if the reduction is carried out with hydrogen.

Fig. 4 shows a sample, reduced 1 hr. with carbon monoxide. The reduction is almost complete, but some small wüstite particles are still left, surrounded by metallic iron. Fig. 5 shows at higher magnification the same sample after etching. The metallic iron, surrounding one of the wüstite particles, consists of almost pure pearlite. At 1000° C. the iron shell therefore consisted of austenite with about 0·8–0·9 % carbon. We know that carbon can diffuse with a great velocity in austenite. In the interface between the austenite and the wüstite the carbon can combine with the oxygen in the wüstite to give a mixture of carbon monoxide and carbon dioxide. From the old manufacture of blister steel by carburizing Swedish Walloon iron, containing big slag inclusions with wüstite as one of the main constituents, we know that gas with a high pressure is formed in the interface between the iron and the slag inclusions, giving rise to big blisters on the surface of the iron.

It is evident that the same phenomenon occurs when we reduce iron ore with carbon monoxide. The gas pressure in the interface between the austenite and the wüstite at 1000° C. can be calculated to be about 40 atm. This pressure seems to be sufficient to separate the iron shell from the wüstite and expand it to fracture, so that the reducing gas can enter through the hole and continue its reducing action on the wüstite (see the upper wüstite particle in Fig. 4).

If the reduction is carried out with hydrogen, iron shells are also formed round the wüstite particles and some of these shells seem to be relatively thick. In this case the iron shells are free from carbon and they seem to obstruct the reduction, so that big wüstite particles are still unreduced after 4 hr. (Fig. 6). Also by the reduction with hydrogen a certain pressure can be obtained in the interface between the iron and the wüstite, if the hydrogen can diffuse inwards through the iron shell and the water vapour cannot diffuse outwards. The partial pressure of the hydrogen in the interface can be equal to its partial pressure in the pores outside the iron shell but the water vapour obtains a higher partial pressure in the interface than in the pores. The difference in the total pressure on both sides of the iron shell can be calculated to be about 0·6 atm., and this is evidently not sufficient to cause a fracture in the iron shell if it has reached a certain thickness. At a high temperature, when the iron atoms have a great mobility, it seems to be easier for the iron shell to reach such a thickness that it can obstruct the reduction than at a low temperature. It is possible that this is the reason why hydrogen can reduce more rapidly at 600° C. than at 900° C.

Another reduction test was carried out with a pure magnetite crystal, a well-shaped octahedron with a diameter of about 2 mm. This crystal was reduced with pure carbon monoxide during 30 min. at 1000° C. In the surface layer metallic iron was produced; in the centre of the crystal unreduced magnetite was left and an intermediate zone consisted of wüstite at the reduction temperature. On cooling, magnetite crystallised from the most concentrated part of the wüstite solid solution.

Fig. 7 shows a section through the porous layer of metallic iron. The interface between the metallic iron and the wüstite is very irregular (Fig. 8). Fig. 9 shows at lower magnification a section through all the three phases, etched with HCl, which has attacked the metallic iron more than the oxide phases. In the upper part of Fig. 9 the unreduced centre of magnetite is visible and, in the lower part, the metallic iron. The zone between Fe_3O_4 and Fe is wüstite, from which small crystals of Fe_3O_4 have precipitated on cooling, partly as a network. In Fig. 10 a part of this net-work is shown at a higher magnification.

The quantity of Fe_3O_4 which is precipitated from the wüstite increases in the direction towards the central unreduced magnetite particle. It is evident from Fig. 9 that no porosity is obtained in the reduction of Fe_3O_4 to wüstite. The transport of the oxygen through the wüstite layer takes place by diffusion in solid solution and the rate of this diffusion seems to be very fast.

As Sir Charles Goodeve has pointed out, it is not necessary to assume that the oxygen atoms diffuse outwards. It is also possible that the smaller iron atoms diffuse inwards, when the oxygen atoms are removed at the outer surface of the wüstite.

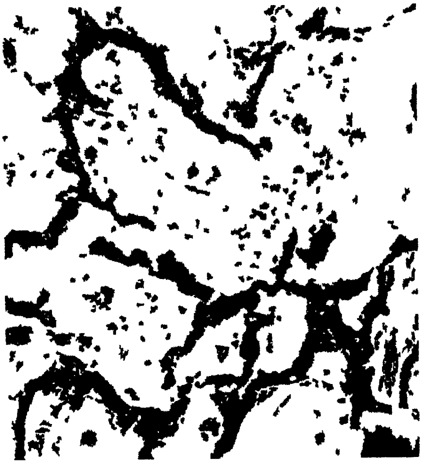

FIG 2—CO 30 min 1000° C (× 300)

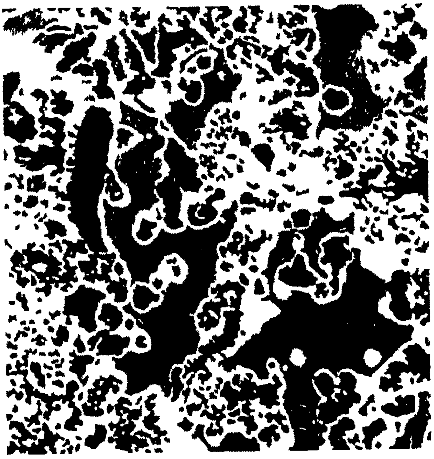

FIG —H 30 min 1000° C (× 300

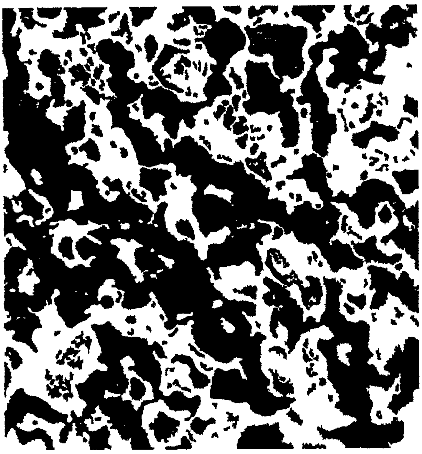

FIG 4—CO, 1 hr 1000° C (× 300 unetched)

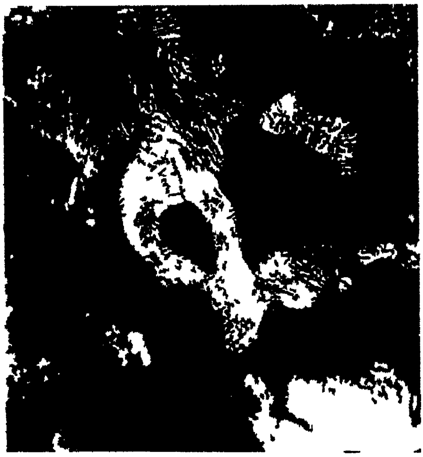

FIG 5—CO 1 hr 1000° C (× 1000 etched)

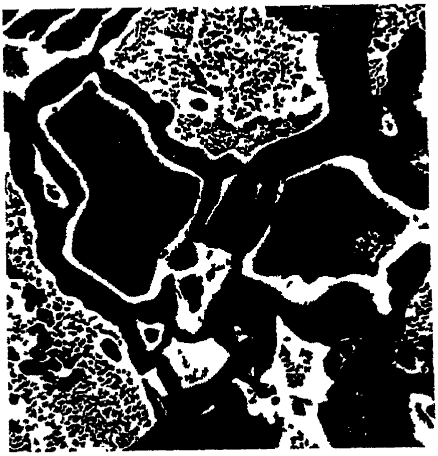

FIG 6—H_2 4 hr 1000° C (× 300)

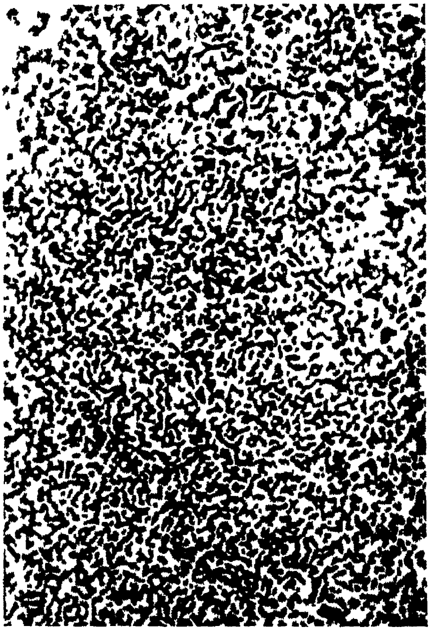

FIG 7.—Magnetite crystal, CO, 30 min, 1000° C Metallic iron and pores (× 500)

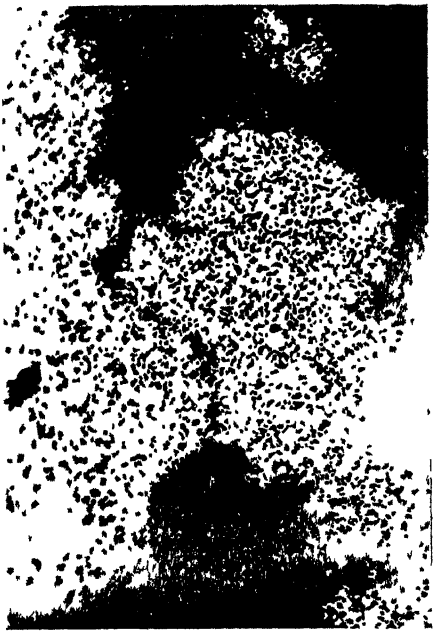

FIG 8.—Magnetite crystal, CO, 30 min, 1000° C Metallic iron, pores and wustite (× 500)

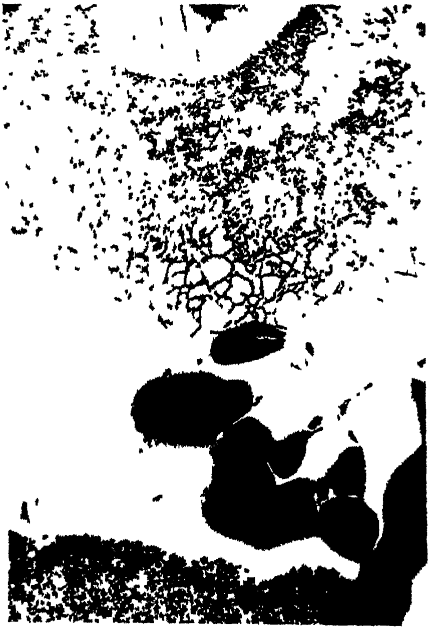

FIG 9.—Magnetite crystal, CO, 30 min., 1000° C. Magnetite, wustite and metallic iron. (× 150, etched HCl)

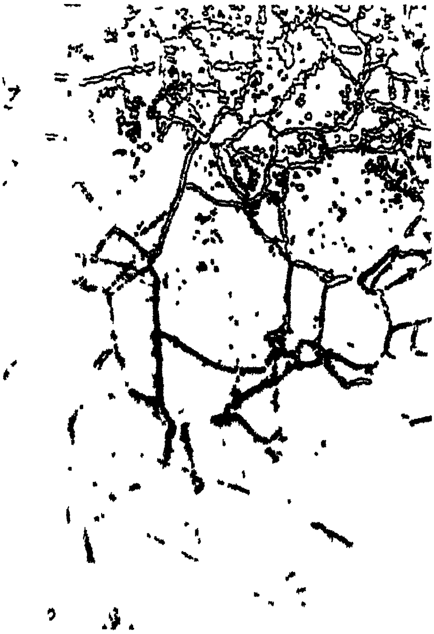

FIG. 10.—Magnetite crystal, CO, 30 min 1000° C. Central portion of Fig. 9, magnetite and wustite. (× 500, etched HCl)

The reduction of iron ore is a complicated process and many details are still unknown. I have shown these pictures to indicate that the microscope can be a useful help in the study of chemical reactions in solid phases.

Mr. R. Wild (*London*) (*communicated*) : Dr. Woods raises a number of interesting points in his paper and it may be worth recording some details of work in progress at Imperial College on the reduction of lump ores in a stream of blast furnace gas (carbon monoxide and nitrogen). Our problem is somewhat more complex because reduction is not being carried out at a uniform temperature but at a temperature which is increasing linearly with time at a rate of 160° c./hr. The experiment is terminated when the temperature reaches 940° c. when the ore lumps, which are cut in the shape of near spheres, are sectioned and analysed to determine the oxygen gradient from surface to centre.

The main object of the work is to determine the relative sizes of various ores which will give similar degrees of reduction at the centre. It is appreciated that heat transfer enters into the picture, but considering the problem from a reduction standpoint the porosity of the ore appears to be the dominating factor. By the use of a gas stream of high velocity the surface film becomes relatively unimportant. Oxygen removal is carried out by a diffusion process which varies with depth, from capillary action near the surface to migration in the lattice near the centre. Whilst the oxygen gradient is nearly linear with depth, fairly well-defined zones may be observed ranging from metal at the surface to predominately ferric oxide at the centre and the higher the porosity the less defined are these successive zones.

Natural magnetites fall into a class by themselves for oxygen removal is very much slower. In general, these materials have a very low porosity and the rate-determining factor is probably the molecular structure.

Mr. H. Herne (*B.I.S.R.A., London*) said : I should like to raise three points on Dr. Woods's paper. Firstly, I want to emphasise a point which Dr. Woods mentions but does not, in my opinion, stress sufficiently, and that is the importance of dynamical similarity in comparing laboratory experiments and full-scale practice. In the paper by Marek, Bogrow and King, from which Dr. Woods takes his data, no attempt has been made to ensure dynamical similarity with blast furnace conditions. The ores they used were almost all screened through 8 to 14 mesh (i.e., were about 1½ to 3 mm. lumps) and the gas velocity through the reaction chamber was about that reckoned to occur in the full-scale blast furnace. This experiment therefore gave a Reynolds number (velocity × characteristic dimension/kinematic viscosity) about 30 times smaller in the experiment than in the furnace. The balance between diffusion in the boundary layer of gas and diffusion in the lump is characterised by a dimensionless group qd/D_s, where q is the material transfer coefficient of the boundary layer, d the characteristic dimension of the lump, and D_s the diffusion coefficient in the lump. These properties refer to carbon monoxide in the experiments quoted but may equally refer to any reducing gas, e.g., hydrogen. From an analogy with heat transfer experience the material transfer coefficient, q, is given by some such relation as $qd/D_g \propto (R_e)^n$ where R_e is Reynolds number and D_g is the diffusion coefficient in the boundary layer ; the best data for heat transfer in beds of broken solids give $n = 1$ as Dr. Woods suggests. The group which measures the balance between diffusion in the boundary layer and diffusion in the lump, qd/D_s, then becomes $R_e \, D_g/D_s$. Assuming that diffusion in the lump is actually diffusion down capillaries $D_s = D_g$ and Reynolds number becomes the simple criterion of the balance between diffusion in the boundary layer and diffusion in the lump itself.

Marek, Bogrow, and King claim, I think without validity, that their experimental results are immediately applicable to full-scale practice. I fear that in a similar way some readers of Dr. Woods's paper may not realise that there is a numerical criterion of the balance between boundary layer diffusion and diffusion in the lump of ore.

The second point is that this boundary layer barrier, having virtually no capacity—in this case, capacity for carbon monoxide or whatever reducing gas is used—acts somewhat similarly to a resistance, if one may extend slightly the "potential" and "capacity" analogy which Sir Charles Goodeve introduced in his introductory paper. But I should not like to continue this analogy with electrical phenomena without further thought as chemical potential are approximately logarithmic with concentration, and diffusion is approximately linear with concentration.

The third point is illustrated by Fig. 4 of Prof. Peretti's paper, "A New Method for Studying the Mechanism of Roasting Reactions." Most of these results give a straight line relationship between time and thickness of reduced material, and, speaking from memory, this kind of result is fairly common in laboratory experiments with iron ores. I presume the mechanism of reduction is by three distinct stages. Firstly, there is diffusion of the reducing gas through the stagnant boundary layer ; secondly, there is diffusion of the gas down capillaries in the reduced solid material ; and thirdly, there is the kinetic process of reduction at the reduced-unreduced boundary. If the first process, diffusion through the boundary layer, is initially the rate-determining one, the network of capillaries built up in the reduced material as the reduction proceeds must behave, in the diffusion problem, like a continuation of the boundary layer. Since the thickness of this boundary layer is generally much less than the size of the lump, the second process, diffusion in the lump itself, must rapidly become the rate-determining one. When this is so, the thickness of reduced material should be proportional, approximately, to the square root of the time rather than to the time itself. This square law relationship is a common experience in many other analogous diffusion problems. The results therefore suggest either that the chemical kinetics at the reduction interface is rate-controlling, or that there is some transport phenomenon in the reduced material other than simple diffusion along a concentration gradient. I should like to ask if anyone can clarify this difficulty.

Prof. B. Kalling (*Domnarvet, Sweden*) said : I should like to say a few words especially in reply to a question put by Mr. Herne, whether the rate of reduction of a piece of ore by a reducing gas is mainly determined by the reaction velocity at the gas-iron oxide interface or by the diffusion rate of the participating gases. It may be of interest to mention that this question was the object of an investigation about 20 years ago in Sweden.[18] At that time it was a rather common opinion that the oxygen transport from the centre of the ore-piece to the surface occurred through diffusion in the solid reduced-iron phase and that the gas diffusion had a more or less negligible influence on the reduction rate. Our investigations showed, however, that this oxygen transport mainly takes place in the gas phase. It was found that at 1100° c., at which temperature most of the tests were made, the diffusion of CO_2 in CO in the gas phase was not only sufficient to take care of all the oxygen but also at this temperature the diffusion rate seemed to be the sole factor determining the rate of reduction from the surface to the centre of the ore-piece. At lower temperatures and when hydrogen was used as reducing gas instead of CO, other factors seemed to retard the reduction. A convincing explanation for this has been given by Prof. Wiberg in his very interesting contribution.

Mr. L. R. Barrett (*London*) said : The parabolic curves expected by Mr. Herne appeared in some work done five years ago[19] on the burning-out of combustibles (sawdust, coals, cokes, etc.) from refractory clay-grog cubes. The cubes of 6 in. side were held for various periods up to 96 hr. in a chamber at 600° c., freely exposed on all sides to air—in motion only by natural convection—at the same temperature. When cool the cubes were halved and the recession of the black core from the surface measured at the centre of the faces. The simple law

$$(\text{Recession})^2 = k\ (\text{Time})$$

was approximately obeyed, in conformity with Fick's law. Some results are shown in Fig. 1. As the core receded to the centre, oxygen approached radially and the curves tended to become straight, rather like those in Fig. 4 of Prof. Peretti's paper, where the direction of flow is also radial.

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[18] Kalling and Lilljekvist, *Tekn. Tidskr.*, 1926.

[19] Barrett, Ford and Green, *Comm. GRB* 9, *Gas Res. Board*, p. 29.

The effect of temperature between 500° and 870° C. was small, the temperature coefficient averaging 1·007. It was shown that the rate of the oxidation reaction was some tenth or hundredth within the brick of that at the surface. The interior was some 50° to 150° C. hotter than the surface, so that a temperature gradient existed in the oxidised envelope.

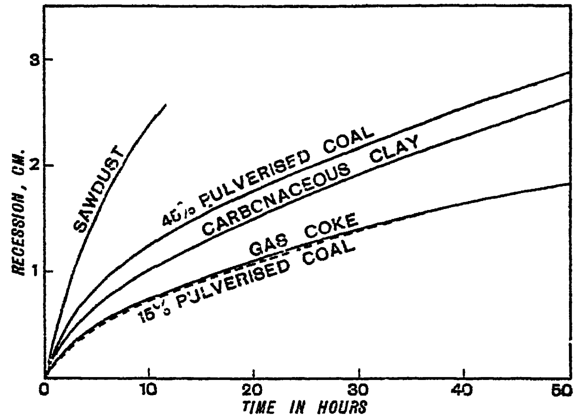

FIG. 1

The rate of recession was higher the higher the porosity but permeability was also a factor when this was very low. Later work[20] on cubes of controlled pore size removed this anomaly for the particular conditions created.

Prof. M. Rey (*Paris*) said : I would like to call attention to two papers which have a bearing on the mechanism of reduction and roasting reactions.

The first one is the study by Ogawa of the roasting of zinc-blende.[21] Using rounded grains of mineral suspended in a stream of air at 800° and 900° C. and reading the decrease in weight of the grain due to the roasting reaction with a thermobalance, he showed that the reaction was controlled by the diffusion of oxygen and SO_2 through the layer of zinc oxide formed. The method might be used in the studies of the reduction of oxides. The second[22] is the work of Neumann, Langer and Köhler who made a study of the roasting of cuprous sulphide by a method very similar to that of Prof. Peretti.

Dr. S. E. Woods (*Avonmouth*) said: With regard to the first point raised by Mr. Herne, I should be sorry if, by too condensed a treatment in the paper, the impression was created that the experimental conditions of Marek, Bogrow and King reflected accurately the behaviour in a blast furnace. In laboratory experiments with beds of ore, the size of particle used is inevitably considerably smaller than in large-scale practice ; to obtain similarity as to the balance between diffusion processes inside and outside the particle it is necessary to increase the linear velocity of gas flow in a corresponding ratio compared with large-scale working. Since such high velocities have not been used in laboratory investigations, the influence of diffusion from the external surface into the gas stream is greatly over-emphasised in these investigations compared with that of the processes occurring within the particle.

The approximately constant rate of recession of the interface between reduced and unreduced (or oxidised and unoxidised) material, commented on by Mr. Herne, can arise even if the process is simply one of diffusion. For diffusion under conditions of spherical symmetry the velocity of recession is inversely proportional to a product $x(1-x)$,

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[20] Barrett and Green, *Comm. GRB* 12.
[21] *Rep. Tohoku Imp. Univ.*, 1929, 9, No. 1.
[22] *Archiv. Metalhüttenwesen*, Band 1.

where x = the fraction $r/(r_0+a)$ and
r_0 = radius of sphere,
r = radius of unreduced portion of sphere,
a = equivalent external gas-film thickness calculated for diffusion coefficient supposed equal to that effective within porous solid.

The range of x with which one is concerned may easily fall within that from, say, 0·25–0·75, in which the product $x(1-x)$ is approximately constant. In addition, the total volume of reacting gas supplied to the system may be so limited that an appreciably higher initial rate of recession may not be possible because during the early stages of reaction the product approaches equilibrium concentrations.

The experiments referred to by Mr. Barrett, with which I was not familiar, provide a very thorough confirmation of a diffusion mechanism analogous to that postulated for iron oxide reduction. The demonstration that permeability was not a controlling factor in itself was of particular interest.

Dr. W. J. Kramers (*B.C.U.R.A., Leatherhead*) (*communicated*): An investigation[23] has recently been made of the factors affecting the rate of conversion of barium oxide into barium carbide by reduction with carbon. The reaction mixture, which consisted of A.R. barium carbonate and shell carbon black compressed into pellets, was heated in an electric furnace in a current of hydrogen. Conversion of carbonate to oxide is rapid at about 1000° C. but it is not possible to obtain reasonably complete reduction of the oxide to carbide below about 1500° C. The reaction is reversible, since if the hydrogen stream is replaced by carbon monoxide, the carbide formed can be completely decomposed:

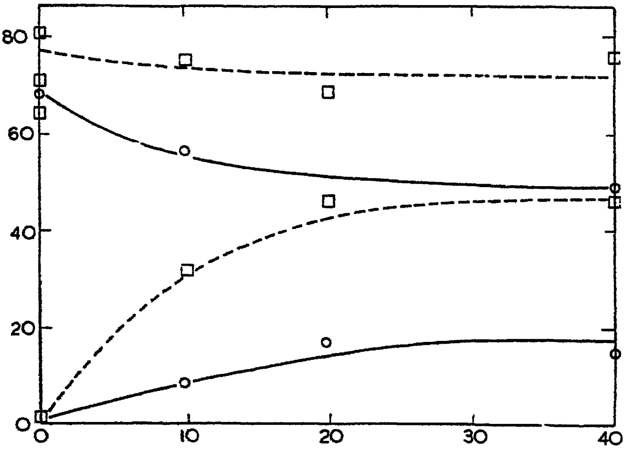

FIG. 1.—Influence of partial pressure of carbon monoxide on yield of barium carbide.

Abscissae: *Minutes*
Ordinates: *Percentage of* BaC_2
——○—— H_2 *containing 25 % CO by volume*
- - - - □ - - - - H_2 *containing 15 % CO by volume*
Temperature: 1500° C. *Furnace*: *Molybdenum.* *Pellets*: ½ *in. diam.*
Scavenging: 300 *l./hr.* H_2. *Mix 47S*

$$BaO + 3C \rightleftharpoons BaC_2 + CO.$$

When the reaction is carried out at 1500° C. in a H_2–CO mixture, it has been found (Fig. 1) that the composition of the reaction pellet appears to approach an equilibrium value in which the proportion of barium carbide decreases with increase in the partial pressure of carbon monoxide. Accordingly, the equilibrium pressure of carbon monoxide is apparently dependent on the composition of the solid phase so that the activities of the components of the latter must be varying. The size of the barium atom is, of course, favourable for the solution of carbon and oxygen atoms in the lattice and the results of X-ray examination favour the view that the products consist of an irregular arrangement of the atoms present.

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[23] Atkins, Pirani, Kramers and Weil, *Coal Res.* (private circulation), Dec., 1946.

The equilibrium proportion of BaC_2 approached from a mixture originally richer in carbide is somewhat higher, probably because the carbon monoxide entering the reverse reaction has in this case to compete with hydrogen for access to the reaction sites. Hydrogen, however, does not appear to play any specific role in the forward reaction since this proceeds similarly in a stream of argon. Below 1500° c. the yield of barium carbide obtainable under hydrogen scavenging decreases progressively with temperature (Fig. 2) and it seems likely that the limiting yield at a given temperature corresponds to the BaO–BaC_2 composition at which the partial pressure of CO has fallen to a negligible value.

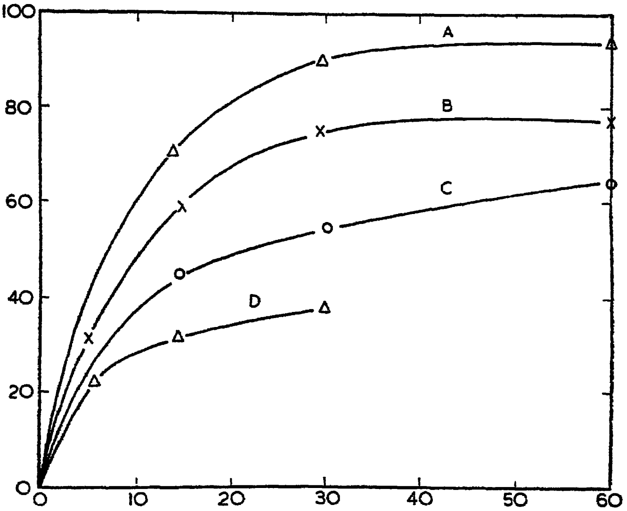

FIG. 2.—Influence of temperature on yield of barium carbide.

Abscissae: *Time (minutes) in furnace at temperature indicated*
Ordinates: *Percentage of* BaC_2 *in reaction product*
Curve A. 1500° c. *Curve B.* 1400° c.
Curve C. 1350° c. *Curve D.* 1300° c.
Mix 47 (20 $BaCO_3$ A.R., 5.4 *shell black*)
Furnace Molybdenum II. Pellets: ½ *in. diam. Scavenging*: 300 *l./hr.* H_2

The influence of departures from stoichiometrical composition in limiting the value of predictions from thermodynamic data has been stressed by Willis and others at this Discussion, but its importance in gas-solid reactions does not seem to have been generally appreciated. Variations in activity in the components of a solid phase are, of course, of particular importance to the practical metallurgist who is usually concerned to effect as complete a transformation as possible of the reacting mixture. Thus, the equilibrium pressure of carbon monoxide in the reaction, $TiO_2 + 3C \rightleftharpoons TiC + 2CO$, has been stated [24] to be one atmosphere at 1039° c. and this is not inconsistent with the knowledge that the reduction commences at 800° c. But it is known [25] that much higher temperatures than 1000° c. and vacuum or hydrogen scavenging are necessary to obtain a high yield of TiC. To avoid misleading conclusions being drawn from equilibrium measurements, it is desirable that the composition of the solid phase should be stated when studies are made on reactions involving more than one solid component.

[24] Brantley and Beckman, *J. Amer. Chem. Soc.*, 1930, 52, 3960.

[25] Brownlee, Geach and Raine, *J. Iron Steel Inst.* (Special Report No. 38) 1947, 75.

Mr. H. Malcor (*Paris*) said: I would like to draw attention to two points in Sir Charles Goodeve's excellent paper. He writes:—

(i) That conditions in the blast furnace are at their best when carbon ceases to react with CO_2 at the highest possible temperature, while the iron oxides cease to react with CO at the lowest possible temperature. It looks quite simple but it means that the old rule insisting upon the need for a highly reactive coke is to be considered now as obsolete. I should like to mention that some experiments we are making now in France seem to substantiate Sir Charles Goodeve's ideas.

(ii) That when two phases are fluid, it is possible to make the simplifying assumption that the surface layer is essentially the same as the bulk, except when the reaction rate at the interface exceeds the diffusion rate to the surface. It seems that in many cases the assumption is too simple and that unhappily the existence of a film at the interface is to be taken into account. It is, for instance, difficult to explain the process in the acid open-hearth practice used on the Continent without supposing the insertion of a silica film between the steel and the slag as Körber and Oelsen did. Moreover, even if diffusion is supposed to be very quick, the composition of a phase at the interface might substantially differ from that of the bulk phase, as any impurity which lowers the superficial tension will accumulate at the interface. This well-known phenomenon might play an important part in the kinetics of heterogeneous reactions.

Prof. M. Wiberg (*Stockholm, Sweden*) said: Dr. Tigerschiöld mentioned the experience at Swedish blast furnaces that the carbon consumption is decreased if a magnetite ore is oxidized to Fe_2O_3 before charging in the blast furnace.

In connection with this I should like to mention that some years ago we made a test at a Swedish charcoal blast furnace with pre-reduced sintered iron ore from Fe_2O_3 to FeO by means of blast-furnace gas in a separate shaft furnace. We did so in order to save fuel in the blast furnace. We did not, however, save any; on the contrary the charcoal consumption was a little higher with the pre-reduced ore than with the ordinary one. The carbon dioxide in the blast-furnace gas decreased more than corresponded to the decreased oxygen content of the ore.

We have also made tests with pre-reduced ore in the manufacture of electric pig iron in low-shaft furnaces, where there is very little gaseous reduction. In this case a considerable saving in fuel and electric energy is obtained if the ore is pre-reduced in a separate furnace.

Dr. W. J. Kramers (*B.C.U.R.A., Leatherhead*) (*communicated*): One speaker has raised the important and difficult question of the assessment of the quality of coke for use in blast furnaces. It was suggested that the coke should not be "too reactive," presumably because high reactivity is often obtained at the expense of mechanical strength. The importance of adequate strength and abrasion resistance in the raw coke has frequently been emphasised, and methods of assessing coke quality are largely based upon empirical tests relating to these variables.[26] However, recent work on the ultra-fine structure of coal and its carbonised products has suggested that other factors, hitherto not taken into account, may be of importance. In particular it has been found that the permeability of cokes to small molecules such as those of the common gases varies critically with the kind of coal used and with the temperature of carbonisation.[27, 28] It is known that this has an important bearing upon combustibility.[29]

In collaboration with Mr. A. M. Adams (B.C.U.R.A.) I have been studying the effect of slow partial combustion upon the physical structure of coke. As reacting gases, we have used both carbon dioxide and oxygen, the coke being maintained at a suitable temperature and the gases diluted with nitrogen. It has been found that with some metallurgical cokes the lumps even when 25 % consumed, have not diminished appreciably in size; there is, however, a significant decrease in crushing strength.

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[26] e g., Thibaut, *Rev. Metall.*, 1943, **60**, 129 (B.C.U.R.A. Trans. Series, No. 57).

[27] Cannon, Griffith and Hirst, *Proc. Conf. Ultra-fine Structure of Coals and Cokes* (B.C.U.R.A., 1944), p. 80.

[28] Franklin, *Coal Res.*, June, 1946, p. 26.

[29] Hirst, *Coal Res.* (in press).

The possible importance of these observations in blast furnace practice arises from the fact[30] that 20–25 % of the coke passing through is consumed under slow combustion conditions in the main body of the shaft where it is particularly important to preserve strength owing to the disintegration of the ores, and the need for having a bed that is freely permeable to gases. If the coke does not change appreciably in size as a result of combustion, the degradation which is observed must be largely the result of mechanical forces in passing down the shaft. The extent of such degradation will be determined not only by the original strength of the coke but also by the degree of weakening brought about by combustion. It is suggested that the decrease in strength of coke as a result of partial combustion may be a factor of importance in assessing the coke quality, and experiments are being undertaken to test this view.

Mr. J. Lumsden (*Avonmouth*) said: There is some doubt about the heat of formation of zinc sulphide. From the figure determined by Kapustinsky and Korshunov[31] for sphalerite,

$$\mathrm{Zn(s)} + \mathrm{S(rhomb.)} = \mathrm{ZnS(s)}\,; \qquad \Delta H_{298} = --48{,}420 \text{ cal.},$$

together with entropy and specific heat data, the following free energy equation is found for the decomposition of zinc sulphide at 1270° K.

$$\mathrm{ZnS(s)} = \mathrm{Zn(g)} + \tfrac{1}{2}\mathrm{S_2(g)}:$$

$$\Delta H_{1270} = +\,91{,}580 \text{ cal.}\,; \qquad \Delta S^{\circ}_{1270} = +\,46{\cdot}98 \text{ cal./deg.}$$

Putting in the condition that the partial pressure of the sulphur is half that of the zinc, the following equation is then found for the apparent vapour pressure of zinc sulphide due to this decomposition in the region near 1270° K.,

$$\log_{10} p_{\mathrm{mm.}} = \frac{-13{,}390}{T} + 9{\cdot}795.$$

It is believed that the observed vapour pressure of zinc sulphide is due chiefly to this decomposition rather than to zinc sulphide molecules in the vapour phase. The same remark applies to cadmium sulphide.

Dr. M. J. N. Pourbaix (*Brussels*) (*partly communicated*): With regard to the statement by Welch concerning the formation of volatile SiO by reduction of SiO_2, and that by Lumsden to the decomposition of ZnS, CdS and CdO, it may be pointed out that the volatility of most metallic oxides at high temperatures seems to be dependent on the formation of gaseous metal or of gaseous suboxide. Only a few metallic oxides, such as PbO, MoO_3 and OsO_4, seem to volatilise without decomposition; several oxides, which were thought to *sublime* on heating most probably behave like HgO, and *decompose* on heating.

For instance, CdO, ZnO, CaO and MgO seem to decompose according to the reactions,

$$\begin{aligned}
2\,\mathrm{CdO}\ \text{(solid)} &= 2\ \mathrm{Cd}\ \text{(gas)} + \mathrm{O_2}\\
2\,\mathrm{ZnO}\ \text{(solid)} &= 2\ \mathrm{Zn}\ \text{(gas)} + \mathrm{O_2}\\
2\,\mathrm{CaO}\ \text{(solid)} &= 2\ \mathrm{Ca}\ \text{(gas)} + \mathrm{O_2}\\
2\,\mathrm{MgO}\ \text{(solid)} &= 2\ \mathrm{Mg}\ \text{(gas)} + \mathrm{O_2}
\end{aligned}$$

and the decomposition pressures of these oxides are approximately given by the relations:

$$\begin{aligned}
\mathrm{CdO}&: \log_{10} P = -13{,}100/T + 7{\cdot}92\\
\mathrm{ZnO}&: \log_{10} P = -16{,}173/T + 6{\cdot}76\\
\mathrm{CaO}&: \log_{10} P = -26{,}605/T + 6{\cdot}53\\
\mathrm{MgO}&: \log_{10} P = -26{,}173/T + 8{\cdot}04.
\end{aligned}$$

The decomposition pressure of HgO may be given by the relation:

$$\log_{10} P = -\ 5227/T + 7{\cdot}43.$$

It is well known that the oxides of alkali metals also decompose with formation of metallic vapour. SnO_2 seems to behave as SiO_2, in the sense that it may form a volatile suboxide SnO.

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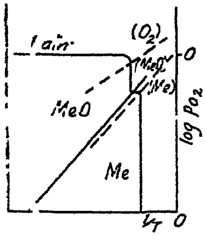
[30] Sarek, *J. Iron Steel Inst.*, 1934, **129**, 97.

[31] Kapustinsky and Korshunov, *J. Physic. Chem. U.S.S.R.*, 1938, **2**, 220.

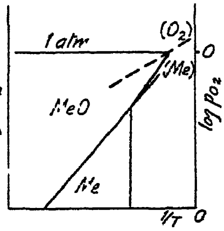
Equilibrium diagrams, such as presented in our paper, easily give information concerning the stability of oxides. If an oxide volatilises without decomposition, its domain of stability is limited by a vertical isobar (Fig. 1); if it volatilises with formation of metallic vapour, its domain of stability is limited by an oblique isobar, this isobar falling vertically in the domain of stability of the condensed metal (Fig. 2); if it volatilises with formation of gaseous suboxide, its domain of stability is limited by an oblique isobar, this isobar having also an oblique branch in the domain of stability of the condensed metal (Fig, 3).

In collaboration with Mme. C. Rorive-Bouté I have tried to establish an equilibrium diagram for the system Sn — O. A particular feature of this system is that, according to calculations made by Veselovskii,[32] gaseous SnO seems to be stable at high temperatures where solid SnO is not stable, and decomposes according to the reaction, $2SnO = SnO_2 + Sn$. Fig. 4 gives an approximate representation of the equilibria for this system. In these four diagrams, the "domains of predominance" of the various gaseous substances have been separated by dotted lines.



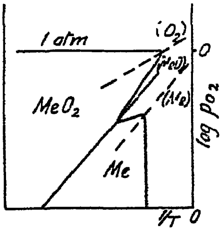
No decomposition. (of Mo)

FIG. 1.



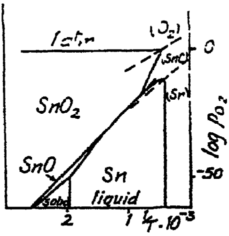
Decomposition with formation of gaseous metal (Hg, Cd, Zn, Ca, Mg, alkali metals)

FIG. 2.



Decomposition with formation of gaseous suboxide (Si, Sn):

FIG. 3.



System Sn-O(approx)

FIG. 4.

It seems that all data given in the literature concerning the volatility of oxides at very high temperatures (especially the data given by Feiser and by Ruff) should be revised. It is very easy to check experimentally whether a given oxide sublimes or decomposes on heating: it may be sufficient to measure, at one temperature, the speed of volatilisation of the oxide in the presence of oxygen and in the presence of an inert gas such as nitrogen. In the first case, the equilibrium condition has the form

$$p_{\mathrm{MeO}} = f(T),$$

and the speed of volatilisation must be approximately the same in the presence of oxygen and in the presence of nitrogen. In the second case, the equilibrium condition has the form

$$p_{O_2} \cdot (p_{\mathrm{Me}})^x = f(T),$$

and the speed of volatilisation must be much lower in the presence of oxygen than it is in the presence of nitrogen.

Dr. O. Kubaschewski (*Teddington*) said: I agree with Dr. Gross that the free-energy formula of zinc sulphide in Kelley's review gives too high values. This is doubtless due to the value of the heat of formation of ZnS which Kelley obtained from early work. This has been redetermined since Kelley's publication by Kapustinsky and Korshunov[33] who obtained by direct combination of pure zinc powder and sulphur a value of $\Delta H_{298} = -48,400$ cal. for zinc blende which is 7000 cal. lower than Zeumer and Roth's value obtained by Mixter's method. The results of the direct method should be more reliable. Using Kelley's calculation and applying the new heat of formation of zinc blende and some other minor improvements in the thermochemical data, I derived independently of Dr. Gross the following free energy formula for the reaction

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[32] *J. Appl. Chem., U.R.S.S.*, 1943, **16**, 397.

[33] Kapustinsky and Korshunov, *J. Physic. Chem. U.S.S.R.*, 1938, **11**, 220; *Acta Physicochim.*, 1939, **10**, 259.

$$[\mathrm{Fe}]_\gamma + [\mathrm{ZnS}]_{bl} = [\mathrm{FeS}]_\beta + (\mathrm{Zn})$$

$$\Delta G = 57{,}200 + 5{\cdot}1\, T \log T - 52{\cdot}50\, T$$

or more simply, for the temperature range in consideration (900–1100° C.),

$$\Delta G = 55{,}100 - 35{\cdot}0\, \mathrm{T}.$$

This is very much closer to Dr. Gross's formula than to the previous one of Kelley's.

Dr. P. Gross (*Stoke Poges*) said : I agree with Mr. Lumsden that Veselovskii's experiments are likely to give the dissociation pressure rather than the vapour pressure of zinc sulphide. The change which this necessitates in the evaluation of the experimental data is certainly not decisive, and the conclusions of our paper remain materially unaffected.

Dr. O. Kubaschewski (*Teddington*) said : I am most interested in the useful work carried out by Pidgeon and King, as I have been associated with similar work done at the Kaiser-Wilhelm Institute, Stuttgart. The results obtained there agree fairly well with those reported in the present paper. The authors have referred to the published work of Schneider and Hesse and stated that there are considerable differences between the vapour pressure values obtained by the German workers and their own values. It should be pointed out, however, that the reactions investigated were different ; the authors used mixtures of silicon with calcined dolomite, whereas Schneider and Hesse used magnesia. In both cases the formation of silicates must be taken into consideration. From an X-ray examination of the final product, Schneider and Hesse concluded that magnesium orthosilicate was formed according to the equation—

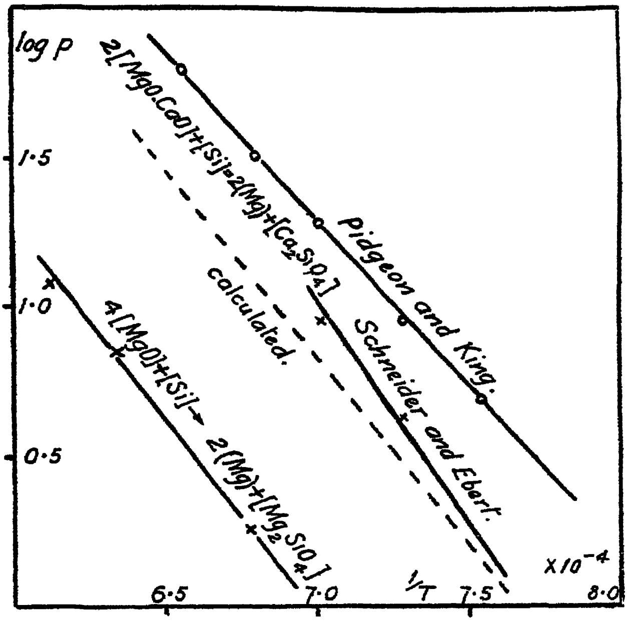

FIG. 1.

$$4[\mathrm{MgO}] + [\mathrm{Si}] = 2(\mathrm{Mg}) + [\mathrm{Mg_2SiO_4}] \quad . \quad . \quad . \quad (1)$$

Where calcined dolomite is used, we should expect a similar formation of calcium orthosilicate,

$$2[\mathrm{CaO}\,.\,\mathrm{MgO}] + [\mathrm{Si}] = 2(\mathrm{Mg}) + [\mathrm{Ca_2SiO_4}] \quad . \quad . \quad (2)$$

Since the free energy of formation of Ca_2SiO_4 from its constituent oxides is about 15 kcal. higher than that of Mg_2SiO_4 the ratio of the magnesium vapour pressures in reaction (2) and reaction (1) must be of the order of ten. This has been established by experimental work carried out by Schneider and Ebert which has not yet been published. The vapour pressure of magnesium over calcined dolomite was in fact found to agree more closely with the values of the present authors (see Fig. 1). If the errors in the method in the two investigations are taken into consideration, the agreement may be regarded as quite satisfactory. The X-ray pattern of the final product showed so many lines that eqn. (2) is probably an over-simplification, and other silicates may have been formed as well. The simultaneous formation of several silicates results in a less reproducible reaction and may be the main source of the remaining differences in the results shown in Fig. 1.

The dotted line in Fig. 1 represents the magnesium pressure of reaction (2) derived from the free-energy formula—

$$\Delta G(2) = +\ 120{,}000 + 11{\cdot}8\ T \log T - 102{\cdot}5\ T \quad . \quad . \quad . \quad (3)$$

which I have calculated from the best data available, neglecting the possibility of a heat of formation between CaO and MgO. The free energy of the formation of calcium orthosilicate was taken from Fig. 3 in Dr. Richardson's paper (this Discussion). The curve calculated for p_{Mg} may be correct within the limits of ± 70 °K. The heat of reaction (eqn. (2)) is found by calculation to be 115,000 ± 4000 cal., exactly half-way between Schneider and Ebert's value (130,000 ± 8000 cal.) and Pidgeon and King's value (100,000 cal.).

All this is no criticism of the authors' experimental work, which I feel sure has been carried out with all care, but it draws attention to the limits of the accuracy which can be expected from the equilibrium measurements and calculations. For practical purposes the mean may be taken between the present results and those of Schneider and Ebert. This involves an error of ± 50° in the range from 1050° to 1250° C.

In obtaining their results, Schneider and Ebert used argon as the transporting gas, but they observed a faster reaction rate when hydrogen was used. The present authors used hydrogen and though the reaction rate should not affect equilibrium values, this may be also a source of the differences observed.

It may be mentioned in this connection that Schneider also tried to measure the reaction pressure of MgO + Si in presence of barium oxide and strontium oxide, in place of calcium oxide. It was not possible to reach equilibrium, probably due to the formation of a layer of impervious substance over the oxide particles. This appears to be in agreement with Pidgeon and King's conclusion that the reaction occurs in the solid state without support by a gaseous intermediary phase. Besides, no mechanism can be imagined which involves a gaseous transfer in the primary reaction.

A higher initial reaction rate was found with powders containing BaO and SrO than with calcined dolomite. This may indicate a higher magnesium pressure, which is to be expected from thermodynamic considerations and from the reasons I mentioned earlier.

Dr. S. E. Woods (*Avonmouth*) said: The following rough calculation indicates that the experiments referred to by Pidgeon and King in the concluding section of their paper, do not provide conclusive evidence that gaseous silicon or silicon monoxide is not an intermediary in the reaction.

The maximum rate of hydrogen passage used was 0·039 cu. ft./min. or 0·0008 mole/sec. The rate at which silicon or silicon monoxide could be carried forward in this stream would then be 0·0008p mole/sec., where p is the vapour pressure of the intermediary expressed in atmospheres.

The mixed charges should contain about 500 cm.^{2} of ferrosilicon surface separated by not more than 0·02 cm. from the surface of dolomite. Diffusion exchange in this system should be about 2Δp mole/sec. (Δp = difference in pressure of intermediate at surface of silicon and dolomite), or some 2000 times greater than the rate of supply in the gas stream. To have provided a conclusive test, it would have been necessary for Pidgeon and King to pass a much greater volume of hydrogen over first silicon and then dolomite, than they appear to have done.

The mobility of a gaseous intermediary is, of course, greatly enhanced at the reduced pressures under which the ferrosilicon process normally operates. A time for complete reaction of a few hours would be possible with a pressure of the intermediary of $10^{-4} - 10^{-5}$ atm. in the presence of hydrogen at 1 atm., or of $10^{-6} - 10^{-7}$ atm. at a total gas pressure of 1/100 atm.

Dr. F. D. Richardson (*B.I.S.R.A.*) said: The results of Prof. Pidgeon and Mr. King give a value of + 18·1 cal. for $\Delta G°$ at 1200° c. for the reaction,

$$2MgO + 2CaO + Si(Fe) \rightarrow 2Mg_{(gas)} + 2CaO . SiO_2.$$

A value for this reaction can be calculated from existing free energy data as follows:

$2MgO \rightarrow 2Mg_{(vap.)} + O_2$	+ 213·0 kcal.
$Si + O_2 \rightarrow SiO_2$	— 145·0 kcal.
$SiO_2 + 2CaO \rightarrow 2CaO . SiO_2$	— 34·5 kcal.
	+ 33·5 kcal.

The difference of 15·4 kcal. seems rather too large to be attributed to a summation of errors in the values used for the calculation, though these might possibly total 8 kcal. A possible explanation may be that at 1200° c. the silicate $3CaO . SiO_2$ is formed since this compound is known to be stable at these temperatures. Such data as exist for $3CaO . SiO_2$ indicate that at 1200° c. its free energy of formation[34] from $2CaO . SiO_2$ and lime is only about 0·3 kcal., but it must be admitted that this is a rather dubious value. It would, therefore, be of great interest to know whether the silicate actually produced in these experiments has been identified by X-rays or any other method. If so, the reaction can be used to add to our present scanty information on the free energy of formation of crystalline silicates.

Dr. J. White (*Sheffield*) said: If I might comment on the point raised by Dr. Richardson regarding the formation of tricalcium silicate, this compound is produced commercially every day as a constituent of so-called "stabilised dolomite." It is not, however, produced very readily from "dry" mixtures, the presence of fluxes and fairly prolonged heating at rather high temperatures being necessary to get anything approaching complete reaction. Further, not only is it unstable above 1900° c. as indicated by the thermal equilibrium diagram, it is also unstable below 1200° c. as shown several years ago by Carlson.[35] The free-energy curve of tricalcium silicate must, therefore, intersect that of the corresponding lime-dicalcium silicate mixture twice, and must be lower than the latter only between 1200° and 1900° c. The free-energy change associated with the formation of tricalcium silicate from lime and dicalcium silicate is probably low, therefore, even under the most favourable conditions, as is the heat value of the reaction. That being so Prof. Pidgeon and Mr. King are probably justified in writing their reaction in terms of dicalcium silicate, at least until they have definite evidence to the contrary.

Dr. P. Gross (*Stoke Poges*) said: During the war, for practical purposes, experiments on the rate of obtaining magnesium from briquettes of magnesia (with and without the addition of lime) or calcined dolomite, and aluminium or ferrosilicon were made. These experiments were not very accurate but were numerous. The majority involved aluminium as reducing agent, but the behaviour of both reducing agents, as observed in these experiments and as inferred from subsequent publications on ferrosilicon, is so similar that there can be very little doubt that the reaction proceeds in both cases in a similar way. The most conspicuous indication that in the case of aluminium the reaction proceeds directly between the condensed reactants is—

(*a*) The rate, within a certain range of particle size, is approximately inversely proportional to the square of the radius of the magnesia particle.

(*b*) The formation of $MgO . Al_2O_3$ is the first product in the reduction of magnesia by aluminium. The formation of $MgO . Al_2O_3$ from the constituent oxides proceeds fast enough for the reaction between the condensed reactants in the reduction to be in no way excluded, and it is influenced by just those factors which one would expect to be decisive on theoretical grounds for reaction between the solids [36]

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[34] Shadduck, *J. Physic. Chem.*, 1937, **41**, 625.

[35] *Bur. Stand. J. Res.*, 1931, **7**, 893.

(*c*) With decreasing powder size the reaction becomes more and more independent of the particle radius. From the activation energy at this stage one is led to conclude that the permeation of the magnesium vapour out of the briquette becomes the rate-determining step. This conclusion is corroborated by a comparison of the observed rate of obtaining magnesium with the calculated reaction pressure together with the measured permeability of the spent briquette for air at low pressure.

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[36] Castell, Dilnot and Warrington, *Nature*, 1944, 153, 653.

III. SLAGS AND REFINING PROCESSES

THE CONSTITUTION AND THERMODYNAMICS OF LIQUID SLAGS

By F. D. Richardson

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Slags of one type or another are used in most pyro-metallurgical operations. In smelting processes they consist of the bulk of the unwanted substances present in the ores, and their composition is adjusted mainly to give a free-running liquid which can readily be separated from the metal. They are usually mixtures of silicates, as is shown by the typical examples in Table I.

TABLE I

Blast Furnace	%SiO_2	CaO	Al_2O_3	FeO	PbO	MnO	ZnO	MgO	Cu_2O
Copper	40	27	6	22	—	0·6	1·4	—	0·5
Lead	32	22	11	33	1	1	4	1	—
Iron	35	44	15	1	—	1	—	3	—

All these slags exhibit certain refining properties, for besides fluxing such unwanted residues as silica and alumina, they remove significant quantities of undesirable elements from the metals themselves. In smelting operations, however, these properties are not of dominant importance, and it is in subsequent refining processes, particularly in the manufacture of steel, that the physical chemistry of slags finds its most important application. Slags are used in the refining of other metals, such as antimony, lead and copper, and take part in a strict sense also in many minor processes such as drossing and liquation. The compositions of some typical refining slags, the more important of which are siliceous, are indicated below in Table II.

The refining of metals by means of slags consists essentially of the transfer of dissolved substances between two liquid phases. It thus relies on chemical reactions at an interface, and the movement of reactants and resultants to and from it. Since these processes involve relatively simple molecules and all occur at high temperatures, their speed is not likely to be controlled by true chemical kinetics. Under these conditions only the highest activation energies could be restrictive. At 1600° c., for example, an activation energy as large as 50 kcal. would lead to extremely rapid reaction with one effective collision in 10^6. This being the case, the refining process may reasonably be pictured as one in which small volumes of slag and metal meet at the interface, where they react and approach equilibrium with each other, and then move apart by convection into the body of the slag and metal respectively. It is to be expected, therefore, that the *rate* of a slag-metal process should, at any instant, be dependent on the extent to which the bulk of the slag and metal are out of equilibrium and the rates at which the participating molecules can move by convection and diffusion in the two media. The importance of the area of the slag metal interface and of convection is shown clearly in the refining of iron and steel. The Perrin process for the dephosphorisation of steel and the normal ladle desulphurisation of iron are completed in a few minutes, whereas the relatively static open-hearth process takes several hours. For practical and economic reasons the slag used in any refining process should be kept to a minimum quantity and should, therefore, have as large a capacity per unit volume as possible for removing the undesirable elements from the metal. In thermodynamic terms the slag should be able to hold a high concentration of these elements at a low chemical potential, and so make possible a favourable partition of them between itself and the metal. The thermodynamics of slags and their viscosities are, therefore, of the utmost importance and it is for these reasons that so much attention has been directed towards them.

TABLE II

Metal Refined	Operating Temp. (° c.)	Type of Slag
Antimony .	900	Soda slag, making an antimony glass containing oxides of Cu, Fe, As.
Copper .	1100	Silicate slag, containing oxides of Fe, Co, Cu, Pb.
Steel . .	1600	Acid Process: Silicate slag, containing oxides of Fe, Mn. Basic Process: Silicate slag, containing oxides of Ca, Al, Mg, Fe.
Iron . .	1300	Desulphurisation: Soda slag to remove sulphur from pig-iron.

It is necessary, however, to understand both why and how a slag works if our fundamental knowledge is to advance, and better slag techniques are to be devised. The development of an adequate molecular picture of liquid slags and of their behaviour is thus quite as important as the measurement of chemical potentials. The earlier workers in this field based their ideas of the nature of liquid slags entirely on their knowledge of the solid state. A later tendency was to formulate the molecular nature of liquid slags, solely on thermodynamic information obtained from slag-metal equilibrium studies. This reaction was almost to be expected since thermodynamics had proved a most powerful means of tackling the chemistry of solutions. It is evident, however, that the full picture can only be obtained by applying both these types of information. In this paper it is therefore proposed to adopt a thermodynamic approach relying on the concepts of chemical potentials and activities, but tempered by existing knowledge of the chemical properties and structures of solid slag components.

The potentials or activities of slag components can be determined from equilibrium measurements of slag-gas or slag-metal systems. The techniques for both types of study are difficult and although it is generally the case that the gas phase is better understood than the metallic solution, so that the gas technique has theoretically a wider application, the difficulties associated with it are frequently the greater. Gas-slag studies have hardly been used, although the method has been generally applied for studying the thermodynamics of pure phases. A vast number of slag-metal equilibrium measurements have been made, but in most cases the slag systems investigated have been so complex as to defy interpretation of the results in general terms. Another possible method is to determine E.M.F.S in slag melts with appropriate electrodes, but this must go hand-in-hand with the development of a fuller knowledge of the ionic constituents of slags to be gained from measurements of electrical conductivities and ionic mobilities. Information on the structure of slags and on the intimate behaviour of the component atoms and molecules has, however, to be obtained by the application of a wider range of physico-chemical methods. This is brought out in the following summary of the main experimental methods which may be employed in tackling the various aspects of the problem and the types of information which may be obtained from them:

X-ray Studies . .	Atomic structure of solid and liquid slags.
Viscosity, Surface Tension	Confirmation of structural picture; indication of presence of long chains, etc.; activation energy for viscous flow.
Electrical Conductivity .	Information on ionic nature of components; activation energy for ion movement.
Electrical Transport .	Information on ionic species present.
E.M.F.S, Slag-gas equilibria, Slag-metal equilibria	Chemical potentials of components.
Thermal Data on Pure Components	Indication of molecular and ionic species likely to be present in liquid from free-energy considerations. Indication of properties to be expected of solutions with compositions corresponding to compounds in the solid state.
Phase Diagrams . .	Indication of molecular species likely to be present. Conditions under which the chemical potential of a component is equal to that of the solid at the same temperature.
Specific Gravity . .	Indication of structural changes in liquid with change of composition.

Slag Structure

The components of slags can all exist as crystalline solids and most of their structures have been thoroughly investigated by X-ray methods. Although the oxides and silicates, of which slags are composed, can be represented stoichiometrically by formulæ of the type FeO, Ca_2SiO_4, etc., they consist, in the solid state at least, of almost infinite three-dimensional molecules in which positive and negative ions are co-ordinated with each other in a continuous lattice structure. The main slag-forming metallic oxides (FeO, MnO, MgO, CaO) are, for instance, all based on a lattice of the sodium chloride type in which each metal ion is co-ordinated with six oxygen ions and vice versa.[1] Their properties are decided to a great extent by the ion sizes, which determine the lattice parameters. In the solid state, a complete range of solid solutions is found to exist between FeO and MnO, FeO and MgO, and between CaO and MnO, but not between CaO and FeO or CaO and MgO. This is to be expected from the order of their ionic radii and lattice parameters.

In a similar way the spinels, of which $FeO.Fe_2O_3$ and $MgO\ Al_2O_3$ are typical examples, must be considered as continuous structures in which oxygen ions, in approximately cubic closest packing, are associated with small positive metal ions.[1] In these cases, however, all the metal positions are not equivalent, for one set of metal ions is co-ordinated tetrahedrally with the oxygen ions and the other set is co-ordinated octahedrally. (The two different sets of positions are, however, not always reserved specifically for the two different types of cation.)

Similar considerations apply to silicates.[2] Here the dominant unit is the tetrahedral SiO_4 group which may share some or all of its corners (i.e., share an oxygen atom) with other SiO_4 groups, depending on the overall silicate composition. In the extreme case, where all four corners are shared, the three-dimensional network of the silica lattice is realised. In the silicates, however, some of the corners are no longer shared, and in silicates where the metal oxides are present in sufficiently high proportions, the silicate tetrahedra exist as independent $(SiO_4)^{4-}$ groups. In all the solid silicate structures, however, the positive metal ions are co-ordinated with a considerable number of oxygen atoms situated at the unshared corners of the SiO_4 groups. Each metal ion is thus linked to a number of silica tetrahedra and the silicate must be considered as a whole, and not composed of individual silicate molecules lying alongside each other. The co-ordination of the metal ions which occur in the solid oxides and silicates depends on their size and charge as indicated by Table III.

TABLE III

Ion	Ion Radius (A)	Co-ordination observed
Na^+	0·95	6, 8
Ba^{++}	1·35	6, 12
Ca^{++}	0·99	6, 7, 8
Mn^{++}	0·80	4, 6, 8
Fe^{++}	0·75	4, 6, 8
Mg^{++}	0·65	4, 6, 8
Fe^{+++}	0·60	4, 6
Al^{+++}	0·50	4, 5, 6

The oxides of aluminium and phosphorus [2] can also occur in tetrahedral groups which also share corners with each other. In the case of AlO_4, even when all the corners are shared, there is one net negative charge associated with the group and this has to be neutralised by a positive metal ion. The PO_4 group, on the other hand, is neutral when it is sharing only three of its four corners. It is this tetrahedral co-ordination of aluminium and phosphorus, which enables their oxides to build so readily into the silicate structures. It is for this reason that phosphorus in solidified basic open-hearth slags appears in a silico-phosphate phase, and it seems a little surprising that the alumina in solid basic slags appears to be present entirely as calcium aluminates.

Our knowledge of the structure of slag compounds in the liquid state is far less satisfactory than in the solid. Very little information is available even on the entropies of fusion of slag compounds, when many of the unreliable values calculated from phase diagrams are neglected. It appears, however, that the entropy of fusion is not unduly high (e.g., $Na_2\ SiO_3\ \Delta S = 9{\cdot}1$, $FeO\ \Delta S = 6{\cdot}1$, $NaCl\ \Delta S = 6{\cdot}7$ cal./degree) so that no major changes in structure are to be expected on melting. On general grounds one would, therefore, expect the liquid structure to resemble the solid, lacking of course the long-range order peculiar to the crystals.

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[1] Bragg, *The Atomic Structure of Minerals* (1937).

[2] Bragg, *The Structure of Silicates* (1932).

The simple oxides might reasonably be expected to behave ideally with respect to each other in the liquid state, when they have comparable lattice parameters and show good solubility ranges in the solid state. This is, in fact, found to be the case for MnO–FeO slags on which careful measurements have been made by Chipman and his co-workers [3] in the course of their phosphorus and sulphur equilibrium studies.

The structure of liquid silicate slags can be inferred more definitely from the X-ray work of Biscoe, Warren [4] and others on glasses. These are supercooled liquids and the systems which have been investigated include silicate, phosphate and borate glasses, over compositions ranging from pure silica to 50–60 mol.-% oxides such as Na_2O, PbO, CaO. The picture of the liquid which emerges is that of a random three-dimensional network made up of SiO_4, PO_4 or BO_3 groups sharing corners with each other. Cations occur in holes in the network and are localised at the unshared corners where there is a negative charge on each of the oxygen atoms common to only one SiO_4 group. As in the crystalline silicates, the cations are co-ordinated with 6–8 oxygens as far as possible. At any temperature the glass has an equilibrium structure dependent on the overall composition. This has been brought out particularly in work on the physical properties (refractive indices and viscosities) of solid silicate glasses, which has substantiated the view that for every composition and temperature there is an equilibrium structure.[5] It is the need for a high co-ordination of the metallic cations, as indicated above, which determines in a large measure the structure and stability of any melt and the chemical potentials of both the oxide and the silica in silicate melts. The effect is seen most clearly in the gap in miscibility which is evident at the silica-rich end of binary systems of metal oxides and silica. As Warren [6] has pointed out, many of these systems break into two immiscible liquids as the silica content is increased, one liquid being almost pure silica and the other relatively rich in the metal oxide. These parts of the phase diagrams for various oxides are shown plotted together in Fig. 1. It will be observed that the concentration of silica at which two liquids are formed increases with increasing radius for the positive ion and decreases with increasing charge. The gap must arise from the conflict between the entropy and energy contributions to the free energy of the system. For

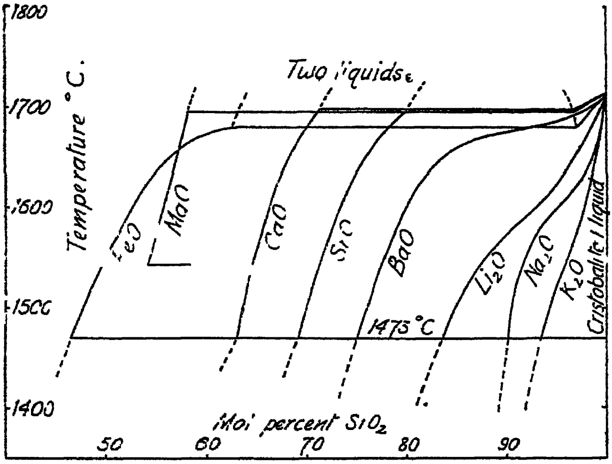

FIG. 1.

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[3] Winkler and Chipman, *Trans. Amer. Inst. Min. Met. Eng.*, 1946, Tech. Publ., 1987. Grant and Chipman, *Trans. Amer. Inst. Min. Met. Eng.*, 1946, Tech. Publ., 1988.

[4] Biscoe, Pincus, Smith and Warren, *J. Amer. Ceram. Soc.*, 1941, **24**, 116. Biscoe and Warren, *J. Amer. Ceram. Soc.*, 1938, **21**, 287.

[5] Douglas, *J. Soc. Glass. Tech.*, 1947, **141**, 64.

[6] Warren and Pincus, *J. Amer. Ceram. Soc.*, 1940, **23**, 301.

the liquid to adopt a state of maximum entropy the two components require to mix completely ; to adopt a state of minimum energy each cation requires to be co-ordinated with six or more oxygen atoms. The oxide of a divalent metal, for example, produces two oxygens suitable for co-ordination for each cation added as oxide. At low concentrations of metal oxide, therefore, uniform dispersion of the cations will lead to co-ordination with only two suitable oxygens, and probably an endothermic heat of solution, offsetting the large entropy. The liquid therefore splits into two phases, one relatively rich in metal oxide and the other consisting of almost pure silica, containing the oxide at a very low concentration. The concentration at which this occurs depends on the increase in the energy of the system when the cations are co-ordinated with two oxygens rather than their normal number. Since ions are almost certainly involved it is to be expected that this concentration will depend on the inter-ionic forces and hence on the sizes and charges of the various cations. The general ionic picture of silicate melts as propounded here is in line with the measurements of electrical conductivity, which is sufficiently high to confirm the presence of ions. An attempt to illustrate this structural picture schematically for an $FeO-SiO_2$ slag is made in Fig. 2.

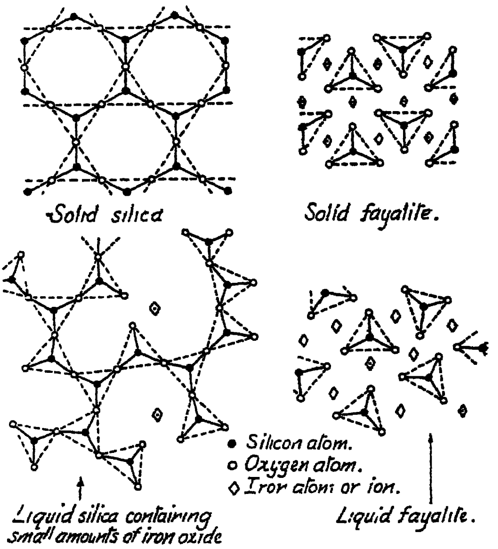

FIG. 2.—Schematic representation of solid and liquid slags. Dotted triangles represent bases of silicon oxygen tetrahedra with apical oxygen atoms omitted. Full lines represent silicon oxygen bonds. In the solid fayalite each iron atom is co-ordinated with 6 oxygen atoms of which 4–5 are shown. In liquid fayalite as drawn each iron is co-ordinated with 5–7 oxygens of which 4–5 are shown.

Before leaving the general subject of ionisation, reference must be made to the very simple ionic treatment which has been proposed by certain authors,[7] and which by a judicious selection of suitable ions has been shown to give equilibrium results in line with actual measurements. In these cases the liquid is usually assumed to consist of various anions and cations and sometimes undissociated neutral molecules. The activities (a) of the various ions are assumed equal to their ionic fractions and the activities of various molecular components as equal to the product of the activities of the relevant ions.

For example in the melt,

$$CaO,\ CaS,\ FeO,\ FeS,$$

the ions would be Ca^{++}, Fe^{++}, $O^{=}$, S^{-},
and the activities

$$a_{Ca^{++}} = \frac{n_{Ca^{++}}}{n_{Ca^{++}} + n_{Fe^{++}}}$$

$$a_{S^{=}} = \frac{n_{S^{=}}}{n_{S^{=}} + n_{O^{=}}}$$

$$a_{FeS} = a_{Fe^{++}} \times a_{S^{=}} \quad \text{etc.}$$

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[7] Tempkin, *Acta Physicochim.*, 1945, **20**, 411. Samarin, Tempkin and Schwarzmann, *Acta Physicochim.*, 1945, **20**, 421. Heinmann, *Bull. Acad. Sci. U.R.S.S.*, 1946, **10**, 1439.

This simple treatment can hardly be of general application. Except in certain special cases the various ions in a molten slag will not be associated equally with the different types of opposite sign, on account of the differences in their energies of interaction, which are determined approximately by the differences in the crystal energies of the corresponding ionic compounds. The success of the treatment in leading to results in line with the measured partition of certain elements, and in particular of sulphur, between liquid iron and slags is almost certainly fortuitous. In the case of sulphur where it has been applied to slags of iron, calcium and manganese oxides, it can be shown that the assumption neither of such equations nor even of ions is essential. The results can be interpreted quite satisfactorily provided the energetics of the substitution of sulphur for oxygen are independent of composition for this particular set of oxides. This may reasonably be expected, since the heat and free energy changes at 1600° c. are approximately the same for all the reactions,

$$\begin{aligned} CaO + \tfrac{1}{2} S_2 &= CaS + \tfrac{1}{2} O_2 \\ FeO + \tfrac{1}{2} S_2 &= FeS + \tfrac{1}{2} O_2 \\ MnO + \tfrac{1}{2} S_2 &= MnS + \tfrac{1}{2} O_2. \end{aligned}$$

Slag Thermodynamics

Little is known directly of the free energies and heats of formation of slag systems. Still less is known of the important chemical potentials of individual components in simple slags. On the basis of thermal data, however, it is possible to calculate the free energies of formation of the various solid silicates, phosphates and aluminates which result from combination between the slag-forming oxides. In the few cases where adequate entropy of fusion data exists, it is possible to extrapolate the solid data to the liquid states, where they can be of great assistance in understanding the behaviour of simple melts and a guide to the types of association likely to be found in relatively complex mixtures. All the available information of this type has been collected and the results are shown in Fig. 3, for those silicates for which reliable data exist. The free energies of formation plotted as functions of temperature are those of the compounds from their component oxides. With the exception of $MgSiO_3$ and Fe_2SiO_4 these have been calculated entirely from thermal data. The most noticeable feature of the diagram is the nearly horizontal form of the free-energy curves, which indicates that in most cases the entropy of formation is very small. In all cases where adequate specific heat data are available, it has been found that the specific heat of the compound above 298° K. is equal to the sum of the specific heats of

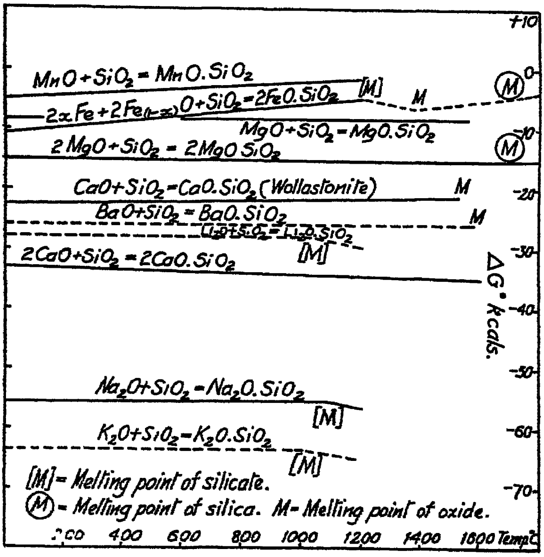

FIG. 3.—Full curves are based on complete or almost complete thermal data. Broken curves are estimates based on incomplete data. Standard states at all temperatures are the stable solid or liquid forms of the pure substances. Since FeO is non-stoichiometric, the standard state taken for it above 570° c. is that in equilibrium with iron at the temperature in question. The equation thus takes the form

$$2x\ Fe + 2Fe_{(1-x)}O + SiO_2 = 2FeO . SiO_2$$

the component oxides within the limits of error of the measurements. It is also generally the case that the heat content ($\Delta H_{298} - \Delta H_0$) of the compound is very nearly equal to the sum of the heat contents of the oxides, and that a similar relationship holds for the entropies. Fayalite is the most noticeable exception, for in this case, $\Delta S_{298^\circ \text{K}}$ is -5 cal./degree, due to the marked maximum in its specific heat at 65° K., which probably accompanies a solid transition. In cases where high-temperature specific heat data are lacking, it has therefore been considered safe to draw the free energy curves on the basis of the values of ΔH and ΔS at 298° K. Where low-temperature specific heat data are not available, a horizontal dotted line has been drawn to indicate the likely free energy of formation, on the assumption of a negligible entropy change. As has already been mentioned, few reliable data exist for the entropies of melting of the oxides and compounds shown, and, with the exception of silica, no specific heats of liquids have been measured. It has therefore only been possible to extrapolate one or two curves into the liquid states by introducing changes of slope corresponding to the entropies of fusion at the appropriate temperature.

The free energies of formation (ΔG) of these compounds can be considered as the sum of the partial molar free energies ($\bar{G}$) of the component oxides. For example:

$$\Delta G^\circ_{\text{Ca}_2\text{SiO}_4} = 2\bar{G}_{\text{CaO}} + \bar{G}_{\text{SiO}}.$$

These separate partial molar free energies are the chemical potentials of the component oxides relative to their pure liquid or solid states according to the standards taken. They are really only of value for the molten compounds where they are a direct measure of the appropriate activities (a) as shown by the equations:

$$(1)\quad \bar{G}_{\text{CaO}} = 2{\cdot}303\, RT \log a_{\text{CaO}}.$$

$$(2)\quad \bar{G}_{\text{SiO}_2} = 2{\cdot}303\, RT \log a_{\text{SiO}_2}.$$

$$(3)\quad \Delta G^\circ_{\text{Ca}_2\text{SiO}_4} = 2{\cdot}303\, RT \log a^2_{\text{CaO}}\, a_{\text{SiO}_2}.$$

As will be seen later, this information, even though approximate, and applicable only to specific compositions, can be of great help in making the most of directly measured activity data when these are available. Another interesting point which emerges from Fig. 3 is the general manner in which the stability of the silicates, relative to their constituent oxides, increases with the size of the positive ion and decreases with its charge. Similar considerations appear to apply to phosphates, and also to aluminates. This relationship between thermodynamic properties and cation size is similar to that shown to exist for silicate melts in the previous section, where it applies to the locations of the miscibility gaps in the phase diagrams, and hence to the forms of the activity curves which may be deduced from them.

Quantitative Behaviour of Two Simple Systems

Since a general view has now been given of solid and liquid slags and slag constituents, it is proposed to consider quantitatively two simple systems in which it is possible to bring structural and thermodynamic information together to form a single picture. It is fully recognised that both the accuracy and the amount of the data available are inadequate for a complete substantiation of the detailed proposals put forward. It is suggested, however, that the picture proposed in each case is as harmonious as possible at the present time.

(1) Iron Oxide containing Ferric Oxide. Ferrous and ferric iron exist together, in the solid phase of iron oxide known as wüstite and also in liquid iron oxide slags. The composition, which is limited in range in the solid state, is determined by the equilibrium oxygen pressure. Solid wüstite consists of an FeO lattice with some of the iron lattice sites vacant, the crystal being kept neutral by the presence of two ferric ions for each missing iron atom. Wüstite may thus be considered as a solid solution of ferrous and ferric ions in an oxygen ion lattice and the equation, representing the enrichment of wüstite with ferric ions in the presence of oxygen, may be expected to take the form

$$2\text{Fe}^{++} + \tfrac{1}{2}\text{O}_2 \rightarrow 2\text{Fe}^{+++} + \text{O}^{=}.$$

At very low concentrations of ferric ions in wüstite, it is also reasonable to expect that the ferrous and ferric ions should behave as an ideal solution in the wüstite lattice. If these conditions apply, it follows that an equilibrium constant (K) should be given by the equation

$$K = (\mathrm{Fe}^{+++})/(\mathrm{Fe}^{++}) \,.\, p^{1/4}_{O_2}.$$

This equilibrium has been studied by Darken and Gurry [8] by means of CO_2–CO gas mixtures. Their results are shown in Fig. 4(*a*), where log ($\mathrm{Fe}^{+++}/\mathrm{Fe}^{++}$) has been plotted against 2 log (p_{CO_2}/p_{CO}); the curves, which almost overlap, have been displaced relative to one another for the sake of clarity. Errors in the measurement of the ion concentrations are almost certainly greatest near the iron-wüstite phase boundary, where small traces of impurity can, under the conditions of their investigation, cause too high values for the ferrous iron. This is the most likely cause of the spreading-out of the curves for the lower temperatures at the lowest ferric concentrations. Within these limits the slope at the lowest concentrations is 4/1, indicating that under these conditions,

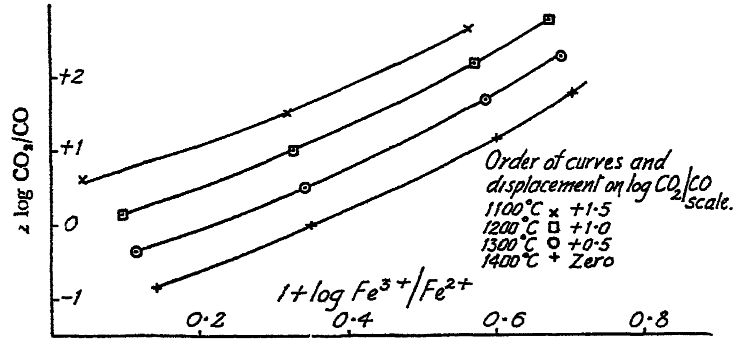

FIG. 4(*a*).

$$\log (\mathrm{Fe}^{+++}/\mathrm{Fe}^{++}) \propto \tfrac{1}{4} \log \left(\frac{p_{CO_2}}{p_{CO}}\right)^2, \text{ and}$$

$$(\mathrm{Fe}^{+++}/\mathrm{Fe}^{++}) \propto (p_{O_2})^{1/4}.$$

It follows that there is some support for the simplification introduced in deriving the equilibrium constant theoretically. Since this can hardly apply at the higher ferric concentrations, the marked departure of the experimental results from this relationship under such conditions is to be expected.*

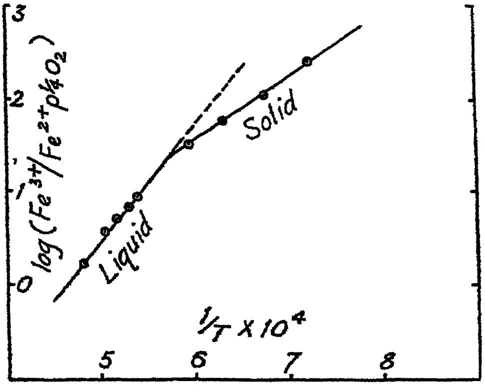

FIG. 4(*b*).

In the solid state, therefore, one has a picture of ferrous and ferric ions in an oxygen ion lattice and not of a mixture of FeO and Fe_3O_4 and Fe_2O_3 molecules, which on structural grounds it would be absurd to consider. It is of interest to see how far this view can be applied to the liquid. In the liquid state at low ferric ion concentrations, which may reasonably be expected to behave ideally, the only data available are those of Chipman and Fetters,[9] who measured th proportions of ferrous and ferric iron in the liquid oxide in equilibrium wit liquid iron at temperatures from 1550°–1850° c. The oxygen pressures in equilibrium with this system can be calculated from the established CO/CO_2 ratio and equilibrium constants (K_{liq}) equal to ($Fe^{+++}/Fe^{++} . p_{O_2}{}^{1/4}$) thus determined The results (only one at each temperature) give a straight line on the log K — $1/$ plot (Fig. 4(*b*)), intersecting the corresponding straight line for the solid at abou 1500° c. The exact location of this intersection cannot be forecast since th wüstites have incongruent melting points, but it is certain that the intersectio must lie above 1369° c. At this temperature solid wüstite is in equilibrium wit solid iron and liquid iron oxide containing a higher percentage of oxygen tha the wüstite. The change in composition is not accurately known, but from th existing phase diagrams it can be calculated that the ratio of Fe^{+++}/Fe^{+} increases from solid to liquid by a factor lying between 1½ and 3. The log against $1/T$ plot shows that at 1369° c., the ratio $(Fe^{+++}/Fe^{++})_{\text{liquid}}$ t $(Fe^{+++}/Fe^{++})_{\text{solid}}$ at equal oxygen pressure is 1·66. Here again the ionic pictur and ionic equilibrium constant are generally in line with established results There seems to be no reason to apply any different picture to the liquid oxid than to the solid and no case for supposing the existence of distinct molecula species such as FeO and Fe_3O_4.

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[8] Darken and Gurry, *J. Amer. Chem. Soc.*, 1945, 67, 1398.

* The matter is considered in more detail in the Addendum.

The liquid system Fe_2O_3–FeO has been studied by White[10] at much highe ferric ion concentrations and correspondingly higher oxygen pressures. Hi measured pressures for various ferric/ferrous ratios are considerably highe than those extrapolated from the values of $K_{\text{liq.}}$ given above. The values o $\log\left(\frac{Fe^{+++}}{Fe^{++}}\right)$ calculated from his results at 1600° c. have been plotted agains log p_{O_2} in Fig. 5, for 1600°, 1650° and 1700° c. Also plotted are corresponding values of log (Fe^{+++}/Fe^{++}) at low concentrations of ferric iron, calculated from the equilibrium constants derived from Chipman's results. It is seen that White's results give slopes which decrease as the (Fe^{+++}/Fe^{++}) increases. It is suggested that at higher ratios still the slope tends to a value of 4/1, as at the lowest ferric concentrations investigated by Chipman, and that the curves over the full concentration range are as indicated by the dotted lines. It seems likely that at the low ferric concentrations the liquid structure resembles that of wüstite, with activity coefficients for all the ions remaining approximately constant. At the highest ferric concentrations it would seem that the liquid structure resembles that of Fe_2O_3 with, similarly, constant activity coefficients for the different ions, so that once again the ratio (Fe^{+++}/Fe^{++}) is proportional to $p_{O_2}{}^{1/4}$. Between these two extreme conditions the liquid has to adopt intermediate structures with varying activity coefficients for the various ion constituents, with the result that the simple proportionality is no longer followed,

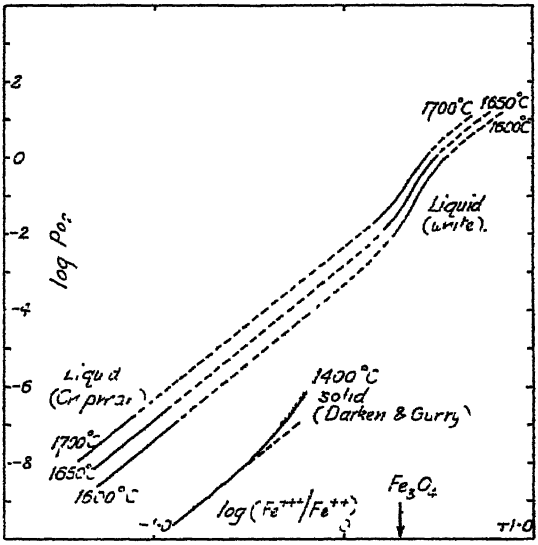

Fig. 5.

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[9] Chipman and Fetters, *Trans. Amer. Soc. Met.*, 1941, 964.
[10] White, *Iron Steel Inst. Carnegie Mem.*, 1938, **27**, 1.

and the equilibrium oxygen pressure changes more rapidly with composition than for either of the extreme structures. It is of interest to observe how the ideality appears to extend from the lowest Fe^{+++} concentrations to the ratio $Fe^{+++}/Fe^{++} = 2$, which is equivalent to Fe_3O_4, before the oxygen pressure changes steeply. This may be connected with the fact pointed out by Goldschmidt [11] that the structures of solid FeO and solid Fe_3O_4 are markedly similar in that each contains the same number of oxygen atoms per unit cube, and that the change from one to the other can be achieved by removal of iron atoms, and minor rearrangements of some of the oxygen and iron atoms remaining.

(2) **Iron Oxide and Silica.** The information available in this system includes:

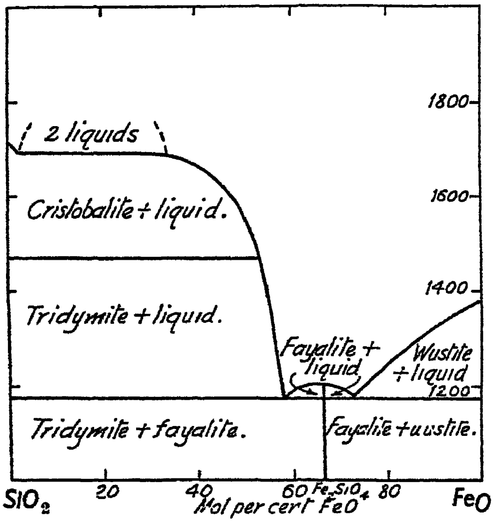

FIG. 6(*a*).

(*a*) the accurately determined phase diagram by Bowen and Schairer [12] shown in Fig. 6(*a*);

(*b*) the crystal structure of fayalite, $2FeO.SiO_2$, as indicated in Fig. 2;

(*c*) the heat of formation of fayalite, from FeO and SiO_2 − 11 ± 2 kcal. at 25° c.,[13] the specific heats of SiO_2,[14] Fe_2SiO_4,[15] and FeO,[16] and the latent heats of FeO[17] and SiO_2.[14] Unfortunately the latent heat of fusion of Fe_2SiO_4 is not known and the thermal data on FeO are poor, so that it is not possible to deduce the free energy of formation of liquid fayalite at 1600° c. with any accuracy. As suggested by the dotted lines in Fig. 3, it may be of the order of − 4 kcal. per mole *;

(*d*) the activities of FeO in FeO–SiO_2 melts at 1600° c. determined by Taylor and Chipman.[18]

From the phase diagram it is possible to determine the activity of liquid silica in the melt over the range of temperatures and compositions where the liquid is in equilibrium with silica. The thermal data for crystalline silica given by Mosesman and Pitzer [14] and for silica glass by Southard [19] were used here, and the results are shown in Fig. 6(*b*). The activity of liquid FeO in the melt was similarly deduced over the range where the liquid is in equilibrium with FeO. These are less accurate than the silica results since the latent heat of fusion of FeO is only known indirectly, and in the absence of suitable data no correction was made for the difference in specific heats between the liquid and the solid. To correct all these values to 1600° c., the partial molar heat of mutual solution of SiO_2 and FeO at the various compositions must be known, though it is to be expected that the curves will approach the ideal more closely as the temperature is raised. For the silica-rich compositions, it would seem that the partial heat of solution of silica is not likely to be endothermic to more than 2–3 kcal. per mole, and the dotted curve for silica has been drawn on this assumption. Chipman's equilibrium studies have shown the activity of FeO to be approximately ideal over the miscible range at 1600° c., a result which is in line with the plotted results and a partial heat of solution exothermic to about 1 kcal. per mole. The high value of the activity coefficient of silica at 43 mol.-%, and the fact that the activity coefficient of ferrous oxide is approximately unity at this composition, indicate that the activity curve for SiO_2 at low concentrations almost certainly follows a course similar to that dotted. This can most readily be appreciated by means of a rough plot of the log of the activity coefficient of SiO_2 against N_{SiO_2}/N_{FeO}, which on appropriate integration gives the log of the activity coefficients of FeO. At the composition $2FeO.SiO_2$, the activities of FeO and SiO_2 are 0·66 and 0·55 respectively, giving values of $-$ 0·15 and $-$ 2·4 kcal. for their partial molar free energies. These combine to give $-(2{\cdot}4 + 2 \times 1{\cdot}5) = -5{\cdot}4$ kcal., for the free energy of formation of one mole liquid fayalite at 1600° c.—a result which is in agreement with the value obtained from thermal data for the free energy of formation of liquid Fe_2SiO_4 from liquid FeO and *liquid silica when the* limits of accuracy are taken into consideration.

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[11] Goldschmidt, *J. Iron Steel Inst.*, 1942, **146**, 157.

[12] Bowen and Schairer, *Amer. J. Sci.*, 1932, **24**, 200.

[13] Troitzsch, *Dissertation* (Braunschweig, 1936).

[14] Kelley, *U.S. Bur. Mines, Bull.* 434, 1939. Mosesman and Pitzer, *J. Amer. Chem. Soc.*, 1941, **63**, 2348.

[15] Kelley, *J. Amer. Chem. Soc.*, 1941, **63**, 2750, and *U.S. Bur. Mines, Bull.* 371, 1934.

[16] Kelley, *loc. cit.*, *Bull.* 371, 1934; *Bull.* 434, 1939.

[17] Richardson and Jeffes, *J. Iron Steel Inst.*, 1948 (in press).

[18] Taylor and Chipman, *Trans. Amer. Inst. Min. Met. Eng.*, 1942, Tech. Publ., 1499.

[19] Southard, *J. Amer. Chem. Soc.*, 1941, **63**, 3142.

* See Addendum, p. 256.

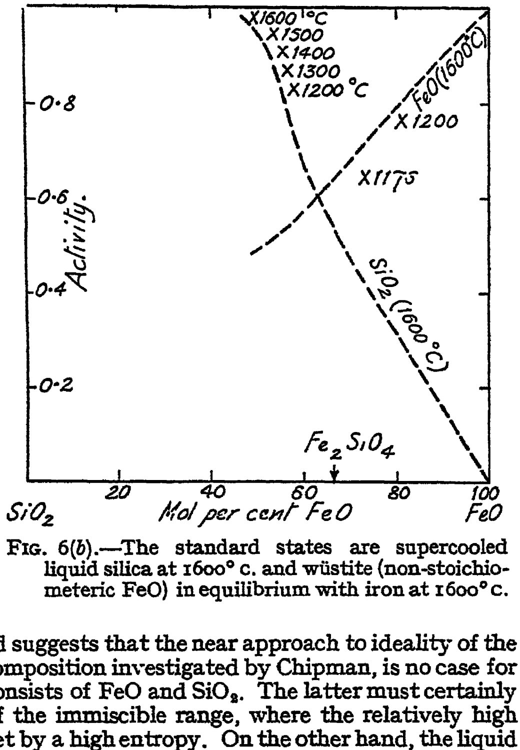

FIG. 6(*b*).—The standard states are supercooled liquid silica at 1600° c. and wüstite (non-stoichiometeric FeO) in equilibrium with iron at 1600° c.

The picture of this melt consisting of Fe^{++} and SiO_4^{4-} ions fits well together and suggests that the near approach to ideality of the FeO activity over the range of composition investigated by Chipman, is no case for his suggestion that the liquid consists of FeO and SiO_2. The latter must certainly exist in the silica-rich liquid of the immiscible range, where the relatively high energy of the system can be offset by a high entropy. On the other hand, the liquid rich in FeO must have a different structure, for the phase diagram shows it to be immiscible with the silica even at much higher temperatures. It is reasonable to suppose, therefore, that it resembles fayalite consisting of ferrous and silicate ions, all of which will be of the SiO_4^{4-} type at compositions containing more than 66 mole % FeO. It is of interest to note that liquid fayalite has a free energy of formation from liquid FeO and liquid SiO_2, which is made up of a reasonably negative heat term (about $-$ 15 kcal. per mole), and a negative entropy. In contrast, the silica-rich liquid almost certainly has a positive heat term and a positive entropy. A point of interest, which is sometimes overlooked in such problems, is that an activity coefficient *greater than unity*—as exhibited by the SiO_2 at compositions rich in FeO—can be accompanied by "compound" formation, provided the free energy of the compound is less than that of the two liquids when homogeneously mixed. Similar curves can be constructed from the phase diagrams of other silica-metal oxide systems. The parallelism between cation charges and sizes and the properties of the melt, previously referred to in Fig. 2, in connection with the miscibility gap, will similarly apply to the activities.

Conclusions

The elucidation of the chemistry of liquid slags is a complex problem, for which it is essential to use all available information on the liquid and solid states concerned. Advances are most likely to come in working from the solid to the liquid states and in treating the liquid as a non-stoichiometric disordered solid with an equilibrium configuration for each composition and temperature.

A knowledge of the structure, behaviour and energetics of the relevant solid phases gives a good indication of structure of the melt and the molecular or ionic species likely to be present. For instance the relation which is seen to exist between cation size and charge and the chemical and physical properties of solid silicates is found to apply also to silicate melts. The solid solubility limits also give an indication as to how slag components are likely to behave with respect to each other in the liquid state. Ideal behaviour is likely to be the exception rather than the rule, so that it is quite unsafe to predict the molecular or ionic species present in a slag melt solely on the basis of activity data and the assumption that ideality applies if the molecular or ionic species are selected correctly. It is more reasonable to interpret activity results in terms of the interaction between the ionic or molecular species deduced from the solid state, it being recognised that a relaxation is to be expected of the solution limits found in solids and that ideal behaviour will be more closely approached as the temperature is raised.

I am indebted to Mr. J. H. E. Jeffes and Mr. G. Withers for valuable assistance and in particular for the calculations on which Fig. 3 is based.

Addendum (*Received 8th November, 1948*).

Dr. T. P. Hoar of the Department of Metallurgy, Cambridge, has called my attention to the fact that, following the work of Wagner and Koch [20] on copper oxide, one would have expected the following equation to represent the equilibrium between ferrous and ferric iron in solid wüstite,

$$2Fe^{++} + \tfrac{1}{2}O_2 = 2Fe^{+++} + O^{=} + \text{vacant cation site } \square .$$

This would give an equilibrium constant of the type,

$$K' = \frac{(Fe^{+++})^3}{(Fe^{++})^2 p_{O_2}^{1/2}},$$

since the concentration of vacant sites is equal to half the concentration of ferric ions. The experimental data, on the other hand, fit the simpler equation proposed in the original paper far better, and the reason for this may be that in the wüstite lattice at these temperatures, it is impossible for a vacant cation site to exist *without* a neighbouring ferric ion, but possible for a ferric ion to exist independently of a vacant site. For this condition the full equation would be

$$2\,Fe^{++} + \tfrac{1}{2}O_2 = Fe^{+++} + (Fe^{+++}\square) + O^{=},$$

and the corresponding equilibrium constant would thus be compatible with the experimental results. The lowest total energy condition for a wüstite crystal containing vacant cation sites is obviously that in which each vacant site is neutralised by *two* neighbouring ferric ions. At high temperatures, where the entropy term in the free-energy equation becomes important, these ferric ion vacant-site complexes may be expected to dissociate, first to vacant sites with one localised ferric ion, and then to free vacant sites. If this is so, one would expect, at the lowest temperatures, an equation of the type,

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[20] Wagner and Koch, *Z. physik. Chem. B*, 1936, 32, 439.

$$2Fe^{++} + \tfrac{1}{2}O_2 = (Fe^{+++} \square Fe^{+++}) + O^{=},$$

and an equilibrium constant,

$$K'' = \frac{(Fe^{+++})}{(Fe^{++})^2 p_{O_2}^{1/2}}.$$

On the plot shown in Fig. *4a*, this would lead to a slope of 2/1 at the lowest ferric ion concentrations, instead of 4/1 and may, in fact, be the cause of the progressive decrease in the limiting slope of the curves as the temperature falls from 1400° C. to 1100° C. In the liquid one may expect an equilibrium equation in which the vacant lattice sites do not figure in view of the large number of holes, which accompany the disorder of the liquid state, and are in no way related to the ferric concentration.

In connection with the thermodynamic treatment of liquid FeO–SiO$_2$ mixtures, it should be stressed that owing to the non-stoichiometry of FeO the full equation for the formation of fayalite from iron oxide and silica at temperatures above 570° C. is,

$$2Fe_{(1-x)}O + 2x\,Fe + SiO_2 = Fe_2SiO_4.$$

The equation relating ΔG° and activities of the various components in liquid fayalite is therefore,

$$\Delta G^\circ_{Fe_2SiO_4} = 2{\cdot}3\,\boldsymbol{R}T \log a^2_{Fe_{1-x}O} \cdot a^{2x}_{Fe} \cdot a_{SiO_2}.$$

As the standard state taken for the iron oxide at each temperature is that in equilibrium with free iron, the value of x will vary slightly with temperature, but will be close to 0·05. Although it appears that this fact was not taken into account in the heat of formation measurement by Troitsch, it is not likely to affect the calculated free energy of formation beyond the limits of error assigned here.

The measurements by Taylor and Chipman on the activities of FeO in FeO.CaO.SiO$_2$ melts, for which the activities of FeO in the binary system FeO.SiO$_2$ can be determined by a short extrapolation at 1600° C., were made in equilibrium with liquid iron. The value of a_{Fe} in the above equation is thus unity, and this permits the check on the SiO$_2$ activity calculated from the value of $\Delta G^\circ_{Fe_2SiO_4}$ at 1600° C., obtained from Fig. 3.

Summary

The present state of knowledge of the structure and thermodynamics of solid and liquid slags and slag constituents is reviewed. The ionic and structural views outlined are applied to two simple liquid slag systems—FeO and FeO–SiO$_2$.

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THE THERMODYNAMIC ACTIVITY OF SILICA AND OF OXIDES IN SILICATE MELTS

By M. Rey

Received 21*st June,* 1948

The behaviour and particularly the reducibility of metallic oxides present in silicate melts are important both from the practical and the theoretical point of view.

Some metallurgists have tried to account for the effect of acidity or basicity of slags upon the reducibility of oxides by assuming that in a fused slag a part of the oxides was free and a part combined as silicates. Only the free oxides were supposed to be reducible. Schenck[1] has based extensive calculations on the idea of free oxides dissolved in an ideal solution, but Körber and Oelsen[2] have refuted his theory in a paper which is one of the most important contributions to this subject. The argument of Körber and Oelsen[2] is as follows: a melt of fluorspar and ferrous oxide separates in two liquids at 1450°. One is fluorspar containing 2 % FeO and the other is FeO containing 2 % fluorspar. The chemical reactivity of ferrous oxide (the authors shun the words thermodynamic activity) must be the same in both phases as they are in equilibrium. It would therefore be necessary, according to the theory of Schenck, to admit that in fluorspar containing 2 % FeO, the percentage of free ferrous oxide is higher than the percentage of total ferrous oxide.

In the field of organic solutions, Dolezalek and his school have tried to explain all the deviations from the laws of ideal solutions by molecular association but this explanation has been proved to be insufficient (Hildebrand[3]). As two liquids forming an ideal solution are completely miscible it is clear that any general interpretation based on ideal solutions is inadequate. This has been clearly stated by Washburn.[4] Recently, however, Chipman and his school have used such concepts in their brilliant studies of equilibria between slags and metals.[5] For example, Chipman has shown that in the system, ferrous oxide—calcium orthosilicate, the oxidising power of the ferrous oxide on liquid steel could be accounted for by assuming that the solution is ideal and that the calcium silicate is associated in groups of two molecules such as $Ca_4Si_2O_8$ (or 4 CaO. 2 SiO_2).

However, as Chipman himself admits, this is more a convenient device for calculation than an actual representation of the molecular state of the solution.

The same association of calcium silicate cannot account for the separation into two liquid layers in the system SiO_2—CaO, nor can a similar association of calcium phosphate account for the separation in the system, ferrous oxide—calcium orthophosphate.

It appears much preferable to make use of the concept of thermodynamic activity exactly as in the study of other solutions. It is also advisable, as far as possible, to consider the activity as a purely thermodynamic quantity, independent of any hypothesis on the constitution of the solution. In this way, any improvement in our knowledge of activities will be a positive step forward and will have a permanent value. Consideration of the actual constitution of the solution should preferably come later as a second step.

Thermodynamic Theory of Solutions

The determination of activities from liquid immiscibility and from melting-point diagrams. It is not possible to go here into the details of the thermodynamic theory of solutions. As is well known, the activity is defined as the ratio of the vapour pressure (or fugacity) of a substance to that of the same substance in a reference state. Usually in non-aqueous solutions the reference state is the pure liquid. Here we shall take the pure liquid as the reference state above its melting point and the pure solid below. We shall call the two activities the liquid and the solid activity.

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[1] Schenck, *Physikalische Chemie der Eisenhuttenprozesse* (J. Springer, 1932 and 1934).

[2] Körber and Oelsen *Stahl Eisen*, 1940, **60**, 921 and 948.

[3] Hildebrand, *Solubility of Non-Electrolytes*, 2nd. Edn. (1936), Chap. IV.

[4] Washburn, *Trans. Amer. Electrochem. Soc.*, 1912, **22**, 333; *J. Amer. Chem. Soc.*, 1910, **32**, 670.

[5] Chipman *et al.* (*a*) *Trans. Amer. Inst. Min. Met. Eng.*, 1941, **145**, 95; 1943, **154**, 228. (*b*) *Trans. Amer. Soc. Met.*, Dec., 1942. (*c*) *Met. Tech.*, Apr., 1946.

At any temperature, the ratio between the two types of activities so defined is given by

$$\log r = \log \frac{a'}{a} = \frac{L}{4{\cdot}575}\left(\frac{1}{T} - \frac{1}{\theta}\right) \quad . \quad . \quad . \quad (1)$$

where a' and a are the solid and liquid activities, L is the heat of fusion and θ the absolute temperature of fusion of the pure substance.

We shall follow the Hildebrand nomenclature and call positive deviation from ideality, the state of a solution where the activity, referred to the *pure* liquid, is greater than the mole fraction ($a > N$) and negative deviation the opposite case. It is well known that liquid immiscibility is a sign of a strong positive deviation, and compound formation a sign of strong negative deviation.

Although this method has received little attention, the solidification curve of a component can give important information on its activity, particularly if it crystallises in the pure state and not as a solid solution. At a temperature T_c along the crystallisation or solidification curve, the activity, referred to the pure solid, is of course equal to unity. Referred to the pure liquid it is given by

$$\log (a)_{T_c} = -\log r = \frac{L}{4{\cdot}575}\left(\frac{1}{\theta} - \frac{1}{T_c}\right) \quad . \quad . \quad (2)$$

At another temperature, the activity is somewhat different. It tends towards the mole fraction, that is the solution approaches ideality, when the temperature increases.

In general the calculation of the temperature correction needs the knowledge of the partial molal heat of solution $\bar{L}_1$. The variation of activity with temperature is then given by

$$\frac{d \log a_1}{dT} = \frac{\bar{L}_1}{4{\cdot}575 T^2} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

This equation can seldom be used because often $\bar{L}_1$ is unknown.

When the solution is " regular " in the sense used by Hildebrand, the temperature correction of the activity referred to the liquid is given by

$$\log \frac{(a)_T}{N} = \frac{T_c}{T} \log \frac{(a)_{T_c}}{N} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

This equation is equivalent to

$$RT \log \frac{a}{N} = \text{constant.}$$

The use of eqn. (2) and (4) permits the calculation of the liquid activity a without requiring the knowledge of the heat of solution. The result is, however, only approximate when the solution is not regular.

The solid activity a' can also be deduced from eqn. (1), (2) and (4) and is given by

$$\log (a')_T = \frac{T - T_c}{T}\left(\log N - \frac{L}{4{\cdot}575\,\theta}\right) \quad . \quad . \quad (5)^*$$

Because (4) has been used in its derivation, this expression is accurate in the case of a regular solution and only approximate in other cases.

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[*] Eqn. (5) is believed to be new. The subject will be detailed in a memoir to be presented before the *Société Française de Métallurgie*.

The Solidification Curves in the Silica-Metallic Oxide Systems

We shall consider the simple systems, silica-metallic oxide. They have been studied mainly at the National Geophysical Laboratory in Washington. The solidification curves are reproduced in Fig. 1, using mole percentages of SiO_2 and oxide as abscissæ.

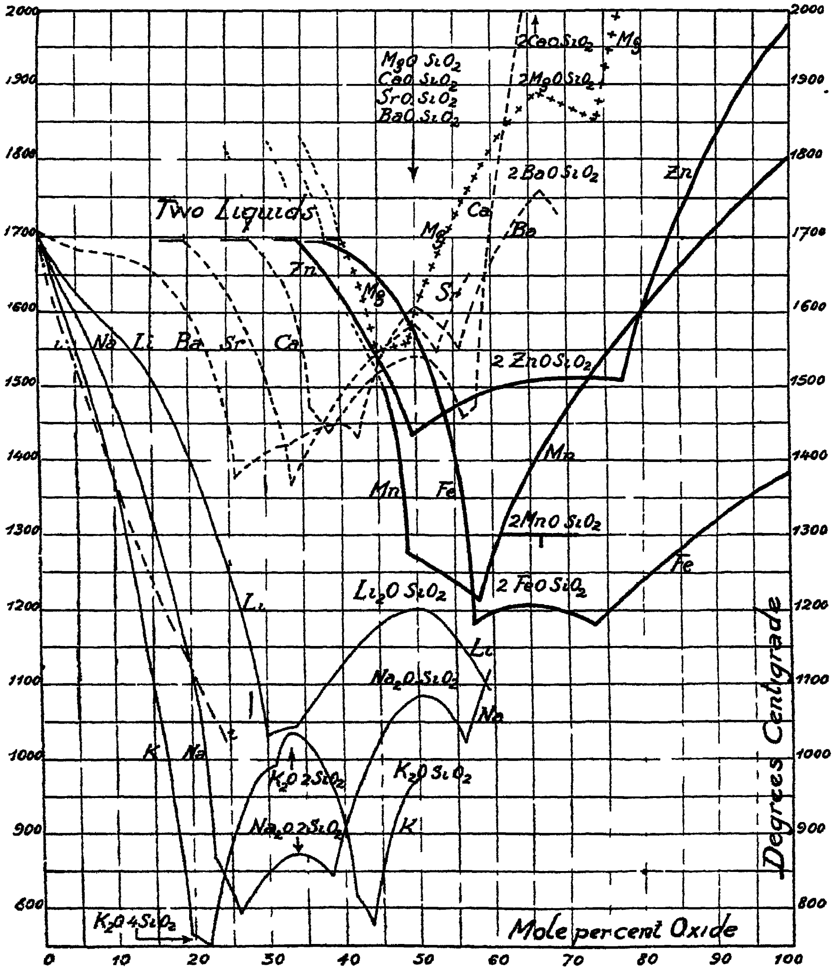

FIG. 1—Solidification curves in binary silicate systems.

Kracek[6] has pointed out that, on the silica side, the various solidification curves of cristobalite form a family whose characteristics vary regularly in the order:

Cs_2O or Rb_2O, K_2O, Na_2O, Li_2O, BaO, SrO, CaO, MgO.

It should be added that MnO and ZnO are intermediate between CaO and MgO and that FeO follows MgO. Cs_2O and Rb_2O form an ideal solution, K_2O and Na_2O show already a slight positive deviation which increases with Li_2O and BaO. With these last oxides the solidification curve of

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[6] Kracek, *J Amer. Chem. Soc.*, 1930, 52, 1436.

SiO_2 shows an inflexion point which is characteristic of a tendency towards separation in two liquid phases. The separation appears in the SrO diagram,[7] increases in the next members of the series and becomes extreme in the case of FeO.

The second important fact about the solidification diagrams is the formation of definite silicate compounds. With the first oxides of the series, giving a nearly ideal silica crystallisation curve, nearly the whole of the field is open for the formation of silicates and there are not only neutral, but also acid, silicates such as Na_2O, SiO_2; $Na_2O.2\ SiO_2$ and even $K_2O.4\ SiO_2$. As the field of silica increases it obliterates progressively the field of acid silicates and even of metasilicates $MeO.SiO_2$ and leaves only the orthosilicates $2\ MeO.SiO_2$. This is shown in the table.

TABLE OF SILICATES

(STABILITY FROM MELTING-POINT DIAGRAMS AND HEATS OF FORMATION)

Silicate index	8	4	2	1
Rb_2O — Cs_2O	$Rb_2O.\ 4\ SiO_2$			
K_2O	$K_2O.\ 4\ SiO_2$ C —	$K_2O.\ 2\ SiO_2$ A 38·4 (2)	$K_2O.\ SiO_2$ B 63·0 (2)	
Na_2O		$Na_2O.\ 2\ SiO_2$ B —	$Na_2O\ SiO_2$ A 68·4 (1)	$2\ Na_2O.\ SiO_2$ C —
Li_2O		$Li_2O.\ 2\ SiO_2$ C —	$Li_2O.\ SiO_2$ A —	$2\ Li_2O.\ SiO_2$ C —
BaO *		$BaO.\ 2\ SiO_2$ C —	$BaO.\ SiO_2$ A 26·7 (1)	$2\ BaO.\ SiO_2$ A 21·7 (3)
SrO			$SrO.\ SiO_2$ A 21·2 (3)	$2\ SrO.\ SiO_2$ A 29·4 (3)
CaO *	Field of crystallisation of silica		$CaO.\ SiO_2$ B 21·6 (1)	$2\ CaO.\ SiO_2$ A 32·6 (3)
MgO			$MgO.\ SiO_2$ C —	$2\ MgO.\ SiO_2$ A —
MnO			$MnO.\ SiO_2$ C 1·46 (1)	$2\ MnO.\ SiO_2$ C —
ZnO				$2\ ZnO.\ SiO_2$ C 12·4 (4)
FeO				$2\ FeO.\ SiO_2$ C 11·3 (5)

(1) In the melting-point diagrams, A = the very stable compounds, the next stable, B. Compounds with non-congruent melting points or a flat solidification curve are denoted by C.

(2) Heats of formation are in kcal./mole of SiO_2, the figures are taken from the following sources: (1) Bichowski and Rossini; (2) Kelley—Contributions to the data of theoretical metallurgy—*U.S. Bur. Mines*; (3) Pascal, *Traité de chimie minérale*; (4) Maier, *U.S. Bur. Mines Bull.*, 324; (5) *Landolt*, III Ergheft, 1936, **3**, 2776.

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[7] Greig, *Amer. J. Sci.*, 1927, **13**, 1 and 133.

* 2 BaO. 3 SiO_2 (C) and 3 CaO. 2 SiO_2 (C) are omitted.

At the same time the stability of the silicates formed varies. This stability can be inferred from the solidification diagrams themselves. As is well known, a pointed solidification curve means a very stable compound, whereas a flat curve means a compound strongly dissociated in the liquid phase. Contributory evidence is given by the heats of formation of the silicates. Both arguments point to the decreasing stability of silicates when going from the alkali silicates to ferrous silicate and to a gradual shift of stability towards the basic side (see table).

A third fact worth noticing is that between the zones rich in silica on one side and the zone of stable silicates on the other, there is a narrow region where silica is still the first solid to crystallise, in the form of tridymite, and where the solidification curve drops very steeply. In the SiO_2-K_2O and SiO_2-Na_2O systems, for example, the curve actually crosses the ideal line. In the case of Li_2O, the curve shows a similar tendency. Other curves become nearly vertical.

Activity of Silica in Binary Silicate Melts

In Fig. 2 we have attempted to show the trend of the activity of silica

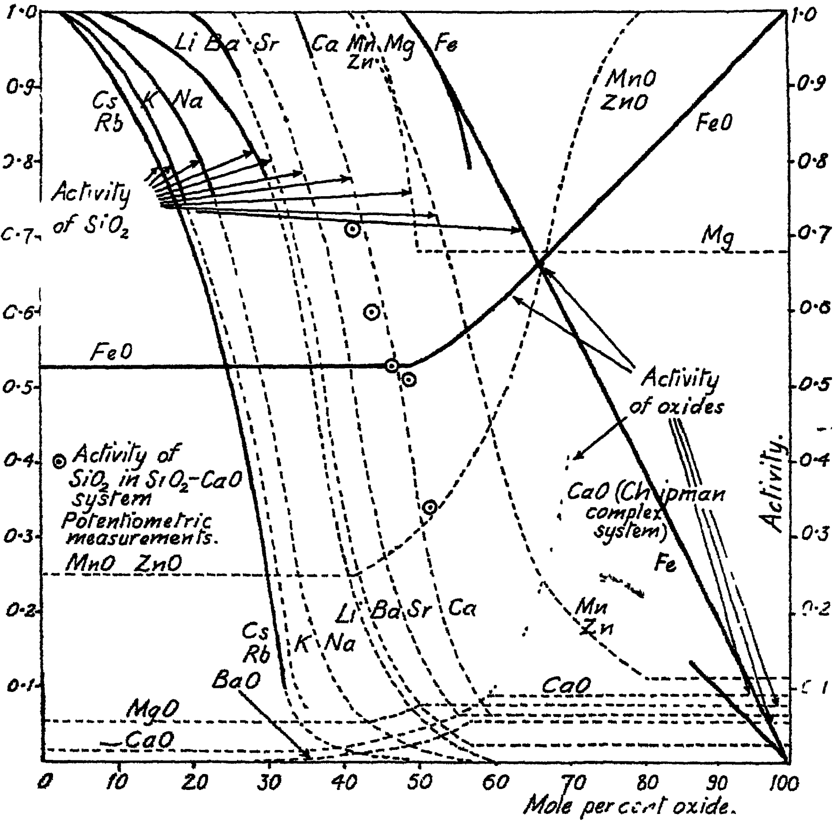

FIG. 2.—Activities of silica and of metallic oxides in binary silicate systems at 1600° C. (solid activities).

in the various systems. The activity is taken in reference to solid silica and the temperature is 1600° C. The activity of silica is unity at the saturation point, so that all the curves begin at unity value.

In the case of Cs_2O, it is not possible to distinguish from the data of Kracek whether the ideal solution of SiO_2 is a solution of SiO_2 in Cs_2O or in a silicate such as $Cs_2O \cdot 2\ SiO_2$. The first hypothesis is untenable as the two materials have a very strong mutual affinity. The second hypothesis must be the correct one.

For any composition of the melt, the proportions of SiO_2 and ($Cs_2O.2\ SiO_2$) can be calculated and the activity of silica taken as its mole-fraction in this system. The curve has been drawn accordingly. For the other systems, eqn. (5) has been used to compute the activity of silica from the solidification curve. The result is only approximate because of the assumptions made in the derivation of the equation. The first part only of the curve can be deduced from the solidification curve. It is drawn as a continuous line. The activity decreases rapidly when drawing away from the saturation in silica and tends towards negative deviation values. There is a certain similarity between the activity curve (at a given temperature) and the solidification curve and a steep solidification curve means a rapid drop in activity. In the region of formation of silicates, the activity of silica and of free oxide must be small when the silicate is very stable and only slightly dissociated, and particularly so when several silicates are formed. This is shown in Fig. 2.

In the case of the SiO_2 — FeO system, Chipman[5b] has shown that at 1600° c. FeO had the same oxidising power on steel as if there was no combination. This means that the solution is ideal for FeO and that the activity of SiO_2 should run as a straight line in the same domain (Henry's law). MnO is more basic than FeO in the SiO_2 — MnO system and the curve should show an intermediate behaviour.

There is an interesting confirmation of the trend of the curve in the SiO_2 — CaO system in a recent paper by Chang and Derge.[8] The authors have succeeded in making a potentiometric determination of the activity of silica in fused calcium silicate and in the ternary system SiO_2 — Al_2O_3 — CaO by dipping into the fused slag two electrodes, one of graphite, the other of silicon carbide. At 1600° c. the authors give five values for the activity of silica at different compositions; these are shown in Fig. 2 and they agree fairly well with the curve drawn.

It is, therefore, a general characteristic of these systems that in a fairly narrow interval of concentration, the activity of silica varies from a very high to a very low value. The main difference between the different systems is the position of this interval. This trend, which is very rarely found in organic or in metallic solutions apparently explains certain influences acting on slag-metal equilibria such as the shift in the value of K_{Mn} (equilibrium constant of manganese) when the ratio of SiO_2 to CaO exceeds equimolecular proportions in the slag.[9]

Activity of Oxides

In simple systems the activity curve of one component can be deduced from that of the other by the use of the Gibbs-Duhem equation. It was hoped to make use of this method in the present case but unfortunately the activity curves of silica are not known with the required precision. However, approximate deductions should be possible and the activity of the oxide should increase rapidly in a certain domain of composition more basic than the composition of the stable silicates.

There is, on the other hand, an important difference between the activity curves of oxides and those of silica. At all temperatures below about

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[8] Chang and Derge, *Met. Tech.*, Oct., 1946.

[9] Krings and Schackmann, *Z. anorg. Chem.*, 1932, **206**, 337.

1700° c. the solution can be saturated with silica so that the activity of silica reaches unity at a certain point. The activity of the oxide is sometimes prevented from reaching unity at the temperature considered by the crystallisation of a given silicate. This is, for example, the case in all the silica-alkaline earth oxide systems where the orthosilicate, or even in the case of BaO, the metasilicate separates out before the solution can be saturated with the oxide. This difficulty in obtaining very basic slags can be surmounted by the admixture in sufficient proportions of Al_2O_3, FeO, or CaF_2 as has been shown by Körber and Oelsen[2] who have insisted on this important point. Fig. 2 attempts to show the trend of the activities of the oxides but unfortunately the curves drawn are very uncertain.

Constitution of Silicate Melts

Warren and Pincus[10] have shown that in the case of alkali and alkaline earth oxides the order of the solidification curves of cristobalite was the same as the order of z/r where z is the valency of the cation and r its radius, this ratio expressing the relative attraction of the oxygen atom for the metallic cation. Dietzel[11] prefers the ratio $\frac{z}{a^2}$, where a is the sum of the radii of the cation and of oxygen. The order of $\frac{z}{a^2}$ and $\frac{z}{r}$ is the same for the alkali and alkaline earth oxides. On the other hand, using $\frac{z}{r}$ the order should be: Ca — Mn (Fe, Zn) Mg, using $\frac{z}{a^2}$ it should be Ca — Mn — Fe — Mg — Zn. None of these sequences accords well with the liquidus lines which show rather the sequence: Ca — Mn — (Zn, Mg) Fe.

This shows that the increasing inability of the various oxides to loosen up the structure of silica and solubilise silica is connected with the increasing attraction of the oxygen atoms for the metallic cations or to the fact that the oxygen is less and less available for entering the silicon tetrahedra and form simple SiO_4^{4-} ions. Dietzel[11] has discussed the subject in detail. It can, therefore, properly be said that iron and similar silicates are strongly dissociated in free silica and free oxide, but this is not in contradiction with the electrolytic dissociation which is manifest from conductivity measurements and electrolysis and it leaves open the question whether the electrolytic dissociation is complete or only partial. If the electrolytic dissociation is complete we should consider a fused sodium silicate as containing SiO_4^{4-}, $Si_2O_5^{2-}$, SiO_6^{4-} and similar ions together with Na^+ ions, and fused ferrous silicate as containing, in addition to the same silicate ions or ions more highly loaded in silica, Fe^{++} and O^{--} ions. The oxygen ions would be prevented from entering the silica structure by the attraction of the Fe^{++} ions.

If the electrolytic dissociation is considered as incomplete, there should be, in addition, molecules of silicate and molecules of free oxide. The various manifestations of the presence of free metallic oxides might speak in favour of partial dissociation. According to Kheinman[12] at 1600° c., fayalite ($2\,FeO.SiO_2$) might contain $2\,Fe^{++}$, $0{\cdot}75\,O^{--}$, $0{\cdot}25\,Si_2O_7^{6-}$, $0{\cdot}16\,Si_3O_9^{6-}$. This corresponds to 37·5 % of the oxygen of the iron oxide as free and 62·5 % combined in the silica anions.

Summary

An attempt has been made to show that the concept of thermodynamic activity is useful, and even necessary, in the study of silicate melts, and that the melting-point

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[10] Warren and Pincus, *J. Amer. Ceram. Soc.*, 1940, **23**, 301.

[11] Dietzel, *Z. Elektrochem.*, 1942, **48**, 9.

[12] Kheinman, *Bull. Acad. Sci. U.R.S.S.*, 1946, 1439; *Brit. Abstr.* 1947, 2674.

diagrams can be used together with data on the stability of silicates and some recent potentiometric determinations to get some idea of the change of activities. The connection between the activity curves and the molecular constitution of the melt has been discussed. It is believed that more precise data might be obtained by vapour pressure determinations of some volatile oxides and in other cases of silica. This work would be worth undertaking.

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THE ELECTRICAL CONDUCTIVITY OF SILICATE MELTS: SYSTEMS CONTAINING Ca, Mn AND Al.

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This investigation into the conductivity of silicate melts has two objects: (*a*) to make measurements relating to the theory of the conductivity of ionic melts which at present exists in substantial form only for simple salts;[1]

(*b*) to study the structure of the systems in the molten state. This object is of additional importance since systems such as $MO - SiO_2$ or $M_2O_3 - SiO_2$ (where M is a di- or tri-valent metal) are the simplest of the systems to which "slags" belong. These systems are still generally regarded as consisting of undissociated oxides[2 3 4] and silicate "compounds" in solution in contrast to consisting of ions. The latter of these hypotheses is indicated by analogy to similar systems [5] e.g., glasses, but experimental proof has been lacking.

Methods of Investigation of $MO-SiO_2$ Systems in the Molten State

The following methods of investigating these systems are possible: (1) equilibrium studies of the distribution of an element between molten metals and molten silicates; (2) density determinations; (3) viscosity determination; (4) X-ray analysis; (5) E.M.F. measurements; (6) electrical conductivity measurements; (7) electrolysis.

Work done on the first of these methods has been regarded as supporting the undissociated oxide theory.[2 3 4] Thus, satisfactorily constant values for K_0, the equilibrium constant for the distribution of Fe between Fe and a slag containing FeO have been obtained on this assumption. In these calculations pure ferrous oxide has been taken as the standard state, i.e., $a_{FeO} = 1$. However, no numerical difference in the calculation of the equilibrium constant in the slag ensues if FeO is totally dissociated, i.e., if

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[1] Frenkel, *Z. Physik.*, 1926, **35**, 652; *idem.*, *Kinetic Theory of Liquids* (Oxford, 1946). Shunsuhe Sisido, *J. Chem. Soc. Japan*, 1938, **59**, 673; 1941, **62**, 381; 1941, **62**, 592.

[2] Schenk, *Physical Chemistry of Steel Making* (London, 1945), 324.

[3] Körber and Oelsen, *Mitt. Kaiser-Wilhelm Inst. Eisenforsch.*, 1933, **15**, 272; Darken, *Trans. Amer. Inst. Min. Met. Eng.*, Tech. Publ., 1942, 1481.

[4] Fontana and Chipman, *Trans. Amer. Soc. Met.*, 1934, **22**, 385; Chipman, *Trans. Amer. Soc. Met.*, 1934, **22**, 385; Fetters and Chipman, *Met. Tech.*, 1941, Tech. Publ, 1316;
Taylor and Chipman, *Trans. Amer. Inst. Min. Met. Eng.*, Tech. Publ., 1943, 1499.

[5] Doelter, *Handb. Mineralchem.*, 1912, **1**, 716; Smekel, *Glass tech. Ber.*, 1929, **7**, 265; Eitel, *Physikalische Chemie der Silikate* (Leipzig, 1929), 95. Muller, *Physik. Z. Sowjet.*, 1932, **1**, 407; Schwarz and Halberstadt, *Z. anorg. Chem.*, 1932, **203**, 365; Lengyel, *Z. physik. Chem. A.*, 1933, **167**, 295; Muller, *Acta Physicochim.*, 1935, **2**, 103; Smekel, *Physik regel Ber.*, 1940 (Ber. 8, Heft 4); Lengyel, *Glass tech. Ber.*, 1940, **18**, 177; Endell and Hellbrugge, ref. 12.

$a_{Fe^{++}} = 1$. Hence, agreement with experiment in these calculations implies either the correctness of the undissociated oxide theory or that of *complete* dissociation into ions.*

A knowledge of the influence of composition and temperature on density is important in the detection of constitutional changes in the molten state [6] and in the calculation of equivalent conductivities.[7] The few determinations available show that, as a first approximation, the volume change on melting or crystallisation can be taken as the same as the difference in the volume of the silicate and its unfused constituents at ordinary temperatures.

A knowledge of viscosity is also important because the viscosity isotherms may give information on the existence of compounds in the melt. Work in this field has aroused some controversy in recent years owing to conflicting experimental results and the position is still unresolved.[8]

The X-ray analysis of silicate melts involves considerable experimental difficulties.[9] It has been shown that silicate tetrahedra exist in various forms depending on the Si/O ratio in the system.

E.M.F. measurements would make possible the elucidation of the activities of components of silicate melts, but it is difficult to find an electrode system which functions satisfactorily in silicate melts (see, however, Chang and Derge [10]). Further, large thermoelectric E.M.F.s arise in the measurements and make deduction of the true, reversible E.M.F. uncertain.

The measurements of the conductivities and electrolysis of silicate melts are free of some of the difficulties of the methods mentioned above and can give definite evidence concerning their constitution. Determination of the energy of activation involved in this process from the temperature coefficient of conductance also gives direct information on the mechanism of current flow.[7]

Results of Previous Work on Conduction of Silicate Melts

Extensive measurements of the conduction of silicate systems have been carried out in the solid state and at lower temperatures (1000° c.). Previous work in the molten state has been mainly technological and *ad hoc* in character [11] and has consisted largely of measurements of complex systems. Measurements of the conductivity of a simpler binary mixture, of which some theoretical interpretation might be possible, are only available in one case.[12]

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[6] Day, Sosman and Hostetter, *Amer. J. Sci.*, 1914, **37**, 1; Lorenzo Hochberg, *Z. anorg. Chem.*, 1916, **94**, 288; Jaeger, *Z. anorg. Chem.*, 1917, **101**, 51.

[7] Bloom and Heymann, *Proc. Roy. Soc. A*, 1947, **188**, 392.

[8] Herty *et al.*, *Min. Met. Invest. Bull.*, 1930, **47**; Endell and Heidtkamp, *Glass tech. Ber.*, 1936, **14**, 89; *idem.*, *Inst Soc. Glass Tech.*, 1938, **22**, 235; Endell and Hax, *Archiv. Eisenhuttenw.*, 1936, **10**, 85; Rait and Hay, *J Roy. Tech. Coll.*, *Glasgow*, 1938, **4**, 252; Preston, *J. Soc. Glass Tech.*, 1938, **22**, 45; Rait, McMillan and Hay, *J. Roy. Tech. Coll.*, *Glasgow*, 1939, **4**, 449; Kozakevitsch, Leyba and Komer, *Conference on Viscosity of Liquids and Colloidal Solution*, *U.R.S.S.*, 1941, 1.

[9] Warren, *J. Amer. Chem. Soc.*, 1934, **17**, 249; *Z. Krist.*, 1933, **86**, 399; *idem.*, *Physic. Rev.*, 1934, **40**, 657; Warren and Loring, *J. Amer. Ceram. Soc.*, 1935, **18**, 269; Warren and Hill, *Z. Krist.*, 1934, **89**, 481; Warren, Crutters and Morningster, *J. Amer. Ceram. Soc.*, 1935, **10**, 30; Schiebol, *Glass tech. Ber.*, 1937, **15**, 231; Beir, *J. Amer. Ceram. Soc.*, 1937, **19**, 339, 347; Hartleif, *Z. anorg. Chem.*, 1938, **238**, 353; Porai-Kosits, *Uspekhi Khim.*, 1944, **13**, 115; Parmalee, Clark and Badger, *J. Soc. Glass Tech.*, 1929, **13**, 285; Clark and Amberg, *ibid.*, 1929, **13**, 290.

[10] Chang and Derge, *Met. Tech.*, 1946, Tech. Publ., 2101.

[11] Farup, Fleischer and Holtan, *Chem. Industrie*, 1924, **12**, 11; Wejnarth, *Trans. Amer. Electrochem. Soc.*, 1934, **65**, 177, and 1934, **66**, 329; Volarovich and Tolstoi, *J. Soc. Glass Tech.*, 1936, **20**, 54.

* It is improbable that it implies *partial* dissociation because the degree of dissociation would then have to remain constant with change of composition of the melt, which is unlikely.

The experimental technique of previous work, where described, is open to substantial criticism. Thus, the use of carbon crucibles and electrodes is objectionable in studying these systems owing to the reaction of C with the slag, admitted to have occurred by Farup, Fleischer and Holtan.[11] Oxidation of the Fe crucible took place in the experiments of Wejnarth,[11] and temperature measurements carried out with an optical pyrometer focused directly on to the surface of the slag [13] are of doubtful validity owing to errors caused by fumes and uncertain emissivity.[10]

Endell and Hellbrugge [12] examined the systems Li_2O-SiO_2, Na_2O-SiO_2 and K_2O-SiO_2 over the temperature range 1250°–1450° C. and the composition range 10–40 % M_2O. A general tendency for specific conductivity ($\varkappa$) to increase with decrease of viscosity (η) was observed. $\varkappa$ increases with ion concentration and a decreasing Si/O ratio.

Martin and Derge,[13] in an investigation of the ternary system $CaO-Al_2O_3-SiO_2$ over the temperature range 1400°–1620° C. and the composition range 35·15–50·1 % SiO_2, 35·1–50·05 % CaO and 5·0–19·7 % Al_2O_3, observed a decrease of conduction with increase of " basicity." The relation reported between $\varkappa$ and composition is complex. For some compositions a plot of log. $\varkappa$ against $\frac{1}{T}$ undergoes sudden changes.

From consideration of the above summary, the work most urgently needed appeared to be the following : (i) systematic measurements of the effect of change of composition in binary systems on the electrical conductivity ; (ii) determinations of the energies of activation of this process ; (iii) the choice of systems should include also ions occurring in " slags." (i) and (ii) require measurements at the highest practical temperatures, so that the largest possible range of compositions may be examined in the molten state ; and so that reliable calculations of energies of activation can be made from a plot of $\log_e \varkappa$ against $\frac{1}{T}$ over as great a temperature range as possible in the liquid state. Measurements have therefore been made up to 1800° C. ; the loss in accuracy incurred by working at the highest temperature is considered to be justified in view of the requirements (i) and (ii).

In agreement with the requirement (iii), the systems examined were: $CaO-SiO_2$, $MnO-SiO_2$ and $Al_2O_3-SiO_2$, in agreement with the relevance of such a study to the constitution of " slags " mentioned above.

Experimental

(i) Materials.—SILICA : Precipitated SiO_2 was unsatisfactory because its bulk before fusion caused the depth of the fused melt in the crucible to be very small. Silica was hence obtained from natural quartz, heated to about 1000° C., quenched, acid-washed to remove Fe_2O_3 and ground in a pestle and mortar of agate.

LIME : CaO was obtained by the ignition of A.R. $CaCO_3$.

MANGANOUS OXIDE : MnO was prepared from A.R. $Mn(COO)_2$ by heating the latter substance to 1000° C. in an atmosphere of forming gas (75 % N_2, 25 % H_2) in a nichrome-wound silica tube furnace. Chemical analysis showed the purity of the oxide to be 97 % (cf., Towers and Gworek [14] who obtained 98·7 %).

ALUMINA : Pure anhydrous alumina was used (Hopkin and Williams).

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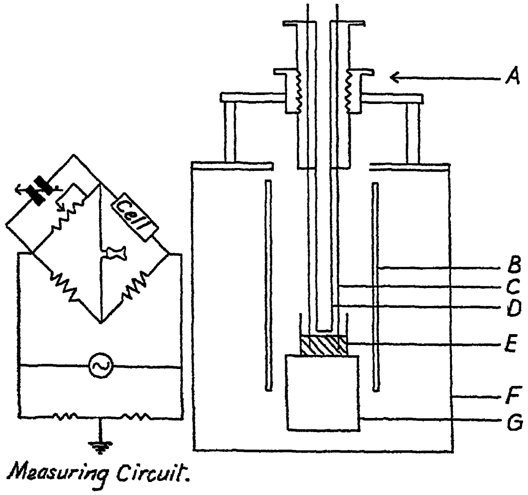
[12] Endell and Hellbrugge, *Naturwiss.*, 1942, **30**, 421 ; *Archiv. Eisenhuttenw.*, 1941, **14**, 307.

[13] Martin and Derge, *Met. Tech.*, 1943, Tech. Publ., 1569.

[14] Towers and Gworek, *J. West. Scot. Iron Steel Inst.*, 1943–44, **51**, 123.

SiO_2, CaO and Al_2O_3 were ignited to constant weight before use. MnO was dried to constant weight.

(ii) **Furnace and Conductivity Cell** (see Fig. 1).—Three furnaces, all metal resistance types, were used in this work and are described in detail in another paper.[15] Most of the measurements reported here were carried out in the tube-type Mo-resistance furnaces. The atmospheres used were hydrogen, argon or forming gas.*



KEY:—

A. Gear for raising and lowering electrodes.

B. Furnace Tube.

C. Molybdenum Electrodes.

D. Molybdenum Sighting Tube.

E. Molybdenum Crucible containing melt.

F. Furnace Case.

G. Alumina Pedestal.

FIG. 1.

The gases were dried by passage through H_2SO_4 and 6 ft.-long tubes containing P_2O_5; the presence of traces of water vapour in the furnace atmosphere was reduced by preliminary heating overnight at 500°–1000° c.

The temperature range examined eliminates the use of a large number of refractory materials (e.g., Pt), otherwise useful for the construction of crucibles. Mo was chosen because of its resistance to the attack of the melts examined in this work. Mo crucibles 2–3″ high and 2″ diam. were made in the laboratory by a welding process.[15] These dimensions were chosen as an optimum to meet the conflicting requirements of the desirability of a large crucible size to increase the measured resistances and of a small crucible size to increase the temperature uniformity of the cell.

The electrodes could be lowered into the melt by means of the arrangement shown diagrammatically in Fig. 1 and described in detail elsewhere.[15] The point of contact of the electrodes with the melt was detected by a sharp change in the resistance between them and this was determined to within about 0·1–0·2 mm. The electrodes were immersed for about 1 cm. in the melt during measurements.

(iii) **Temperature measurements** were made with optical pyrometers of a special design [15] sighted on the closed end of a molybdenum tube 2–3 mm. above the surface of the slag.[15] The absolute accuracy of these temperature measurements by this means up to 1650° c. was found to be ±5° by comparison with a Pt/Pt–Rh thermocouple and the self-consistency among three different observers up to 1800° c. had the same limits, which must be considered satisfactory. The change in measured temperature at about 1700° c. between a point 3 cm. above the surface of the melt and 1·5 cm. below it was about 10° c. which is satisfactory considering the difficulty in achieving a uniform temperature at the temperatures used.

[15] Kitchener and Bockris, This Discussion.

* Only forming gas or argon was used for measurements in the system MnO–SiO_2 owing to the possibility of reduction with hydrogen (see above for method of preparation of MnO). The effect on the results of the different atmospheres used was within the experimental error.

(iv) **The electrical circuit** consisted of a Wheatstone capacitance-resistance bridge, the capacitance being in parallel with the adjustable resistance of the bridge. The bridge circuit was connected with a Wagner earth.[19] A beat frequency oscillator was used with a frequency range of 500–10,000 c./sec. and an output of 1·6 w. The frequency normally used was about 1000–1500 c./sec. and of pure sinusoidal form. Earphones were used and the detection of sound minima was facilitated by use of a sound-proof cabinet. (Reproducibility of balance point on a given melt under apparently constant conditions was 1 %.) The A.C. furnace heating-current was induced into the bridge circuit (the electrodes being at a potential of about 150 v. when the furnace was "on") and this provided a background noise in the earphones so that the furnace current was switched off during measurements.

A conventional rule,[16] valid for aqueous electrolytic solutions, states that to eliminate polarisation the area of the electrodes must be $>10/R$ sq. cm. in area, where R is the resistance to be measured. This rule could not be followed because the electrodes required would have an area of 10–100 sq. cm. which was not practicable. Further, it was not possible to use one of the walls of the metal crucible as one electrode [18] because this would have made the resistance of the cell at the highest temperatures too small to take measurements of value.[18] Molybdenum rods about 0·2 mm. thick were hence used as electrodes. The cell constant was measured at room temperatures, the cell being filled to various depths with 0·1 N. KCl solution.

At the highest temperatures the resistance between two most distant points on the crucible was 6×10^{-3} ohm. This was always at least 10 times less than the minimum resistance of the most highly conducting slag. It can be shown that under these conditions the net cell constant should be independent of concentration, i.e., of the composition of the electrolyte, so that the cell constant obtained by measurements with the aqueous solution could be used for measurements with the silicate melts, without spurious effects due to conduction through the sides of the crucible.

Measurements of the cell constant were carried out at different depths of immersion of the electrodes because owing to the effect of the conducting bottom of the crucible, the cell constant is not proportional to the depth of immersion, unless the electrodes are more than 1·8 cm. above the bottom.

The effect of temperature on the cell constant is difficult to calculate because it includes effects due to the expansion of the electrodes, the temperature gradient along which is not accurately known, the expansion of the crucible and the expansion of the slag. The net expansion was therefore obtained empirically by determining the point of contact of the electrodes with the melt at various temperatures. Over the temperature range 1200°–1700° C. it was found to vary by 0·18 cm.

The resistance of the molybdenum electrodes and other leads was measured in the cold and from this the maximum value was found at 1800° C. by calculation on the assumption that the whole length of the electrodes was at this temperature (0·01–0·02 ohm).

Hence,

$$\varkappa = \frac{C_{r_1r_2}}{R-l}$$

where $C_{r_1r_2}$ is the cell constant for a given depth of the melt (r_1) and depth of immersion of electrodes (r_2) ; R is the apparent net resistance and l the resistance of the leads.

(vi) **Tests for Electrolytic Polarisation.**—Electrolytic polarisation generally decreases with increasing temperature and was expected to be small at the high temperatures used. This was tested experimentally in two ways. The conductivity of a 65–35 % CaO—SiO$_2$ mixture was measured at 1650° C. (*a*) for various depths of immersion of the electrodes and (*b*) for various frequencies between 500 and 10,000 c./sec. When allowance was made for the change of cell constant with depth of the electrolyte mentioned above, the conductivity was found to be approximately proportional to the area immersed, thus indicating the absence of polarisation. (The cross-section of the electrodes was of negligible area in this context.) In support of this, change of frequency under the conditions mentioned affected the conductivity by <1 % at about 1650° C.

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[16] Kohlrausch, *Leitvermögen der Electrolyte* (Leipzig, 1898), 11.

[17] Cuthbertson and Waddington, *Trans. Faraday Soc.*, 1936, **32**, 745.

[18] Jaeger and Kapma, *Z. anorg. Chem.*, 1920, **121**, 27.

[19] See Jones and Joseph, *J. Amer. Chem. Soc.*, 1928, **50**, 1049.

(vii) **General Procedure.**—The dry components are mixed in appropriate proportions and shaken in an air-tight dry glass vessel for about 1 hr., or agitated in a ball mill to ensure homogeneity. The crucible containing the powdered mixture is placed on an alumina pedestal in the middle of the furnace tube, the furnace sealed and the temperature raised in the course of some hours to 1750° C., this temperature being maintained for about one hour to ensure homogenisation and the elimination of bubbles from the melt. After determining the position of the slag surface, the electrodes are inserted to a depth of 1 cm. in the melt, the furnace current turned off and readings of conductivity and temperature taken during cooling. Readings are continued until the temperature is well below the m.p. of the material under examination, and then the run is repeated whilst the temperature is increased up to 1800° C, the furnace current being switched off when readings were being taken. In some measurements, a few seconds elapsed between readings of conductivity and temperature and this may add about 3° C. to the uncertainty of the temperature reading.* A new molybdenum crucible is used for each experiment.

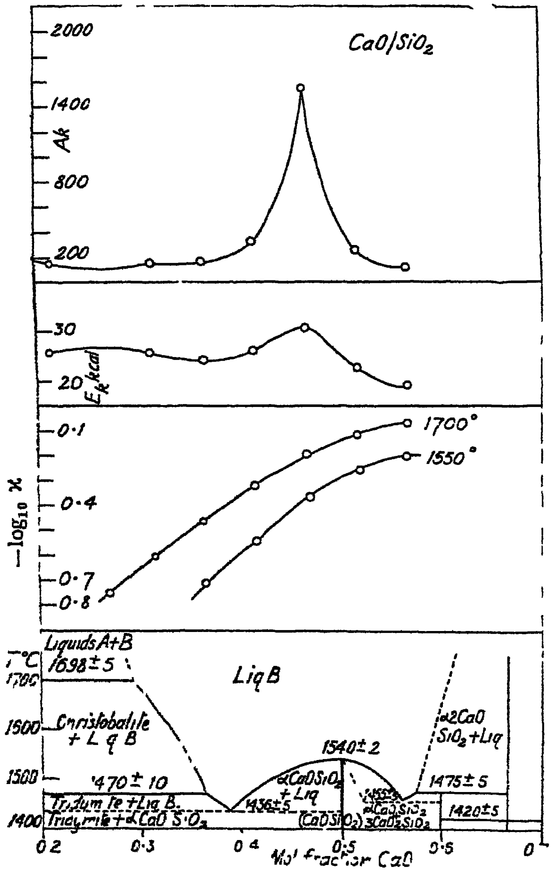

FIG. 2.

(viii) **Accuracy of Measurements.** — The accuracy of the measurements is low when compared with that of good work on molten salts at temperatures $<1000°$ C.[18] The three main causes of this are: (i) creep of the melt up the Mo electrodes may change the effective cell constant; (ii) the distance between the electrodes can be obtained only to within 1 mm. in about 25 mm.; (iii) at the highest temperature for some slags the resistance to be measured falls slightly below 0·1 ohm and the accuracy of determination of such resistance by a Wheatstone network is not high.

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* The rate of cooling of the system was about 10°–20° per minute for the temperature range 1800°–1700° C.; the total time taken for the system to cool from 1800°–1000° C. was about 4–5 hr. in a forming-gas atmosphere.

The reproducibility of $\varkappa$ was about ± 5 % in the liquid state and somewhat less in the neighbourhood of the m.p., where very small variations of temperature cause large variations in conductivity.

Results

Representative results * are shown in Fig. 2–9 and in Tables I–IV. Results reported are essentially for the molten state only. The composition ranges quoted are those which are liquid over an appreciable range above the temperature 1600° c.

TABLE I

COMPARISON OF CONDUCTIVITIES OF VARIOUS SYSTEMS AT 1700° C.

System	Approx. Composition Studied (Mol frac. MO or M^{-+})	$\varkappa_{1700}$ (mhos)
$CaO-SiO_2$	0·25–0·44	0·2–0·9
CaO	1·00 (extrap)	3 (extrap)†
$CaCl_2$	1·00	5 (extrap)‡ (1·99 at 800° c.)
$MnO-SiO_2$	0·35–0·8	0·6–9·5
MnO	1·00 (extrap)	10 (extrap)†
$Al_2O_3-SiO_2$	0·01–0·06	0·0006–0·004
$AlCl_3$	1·00	0·05 approx. (extrap)
KCl	1·00	4·1 (2·19 at 800° c.)

† Extrapolated in from experimental data of this paper at 1700° c.

‡ Extrapolated to the hypothetical value 1700° c. according to the formula given by Drossbach.[20]

Some initial measurements were carried out on the typical system CaO, Al_2O_3, SiO_2, which had been examined by Martin and Derge. Substantial agreement (the discrepancies varying with composition from 3–10 % at 1600° c.) was obtained with the results of these authors.

The specific conductivities of the $CaO-SiO_2$ and $MnO-SiO_2$ systems are high (see Table I), and greater than that of a normal solution of a strong electrolyte at ordinary temperatures (e.g., for a N. aqueous KCl at 25°, $\varkappa$ is 0·11 mhos). The extrapolated (hypothetical) conductivity of CaO at 1700° c. is of the same order as that for $CaCl_2$ at that temperature. The extrapolated (hypothetical) value for MnO is somewhat greater. The conduction of the $Al_2O_3-SiO_2$ system is lower than that of $AlCl_3$.

There is a general increase of conductivity with concentration of MO for $CaO-SiO_2$ and $MnO-SiO_2$ (Fig. 2 and 3 and this is also in itiallytrue for $Al_2O_3-SiO_2$ (Fig. 3). Two conductivity isotherms are shown for each system respectively (Fig. 2, 3 and 4), one at 1700° c. and the other at the lowest temperature in which a substantial composition range remains molten. In $CaO-SiO_2$ and $MnO-SiO_2$, no minima occur in these relations, which pass through the composition corresponding to the compounds existing according to the phase diagrams in the solid state, without significant inflection.

The conductivities increase exponentially with increase of temperature (Fig. 5, 6 and 7). The slope of the plots of log $\varkappa$ against $\frac{1}{T}$, linear for considerable temperature ranges, undergoes inflections in some systems.

In the neighbourhood of the melting point the variations of conductivity with temperature are complex and will not be described in detail until a fuller investigation has been completed. The typical sudden decrease in conductivity (shown in Fig. 8) took place below the m.p., according to the phase diagram. Measurements taken on heating in this region showed hysteresis, the conductivity being lower on heating than on cooling up to approximately the melting point.

Comparison between conductivity and viscosity can be made over only short ranges of composition * (Fig. 9). A parallelism between fluidity and conductivity exists but conductivity decreases more rapidly with increase of Si/O ratio than does viscosity increase.

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[20] Drossbach, *Elektrochemie geschmolzener Salze* (Berlin, 1938), 72.

* Not all those points which compose a continuous relation are exhibited in the figures, in order to preserve clarity.

Preliminary attempts at electrolysis in the system $CaO-SiO_2$ (35–65 %) were carried out at 1450° C. They were discontinued owing to difficulties in finding a suitable electrode system. (The molybdenum anode dissolved on passage of current; C electrodes are attacked.) After electrolysis for about 1 hr. at a current of 2 amp., some whiteness appeared in the neighbourhood of the anode. It is possible that this indicates the anodic formation of SiO_2 (cf., Martin and Derge [15]).

TABLE II

CONDUCTIVITY, VISCOSITY AND ION-OXYGEN PRODUCT OF 1/1 M_2O-SiO_2 AND $MO-SiO_2$

System	Radius of Cation	Ion-Oxygen Attraction $\times 10^{-16}$ E.S.U.	$\varkappa_{1300}$ (mhos)	η (approx.) (poises)
$MnO-SiO_2$	0·91	0·81	0·53	2
$CaO-SiO_2$	1·10	0·69	0·18	16
Li_2O-SiO_2	0·78	0·45	0·12	6
Na_2O-SiO_2	1·10	0·35	0·07	4
K_2O-SiO_2	1·39	0·27	0·16	1

(ix) **Comparison with Previous Work.**—The only comparable measurements are those of Endell and Hellbrugge.[12]† A quantitative comparison between the present results and those for the M_2O-SiO_2 systems is given in Table II for the 1/1 ratio at 1300° C. Comparative values of viscosity and of what may be called "ion-oxygen attraction," i.e., the quantity $2\frac{z}{r^2}$ (where z is the valency of the cation, and r the distance between the centre of an M ion and an O ion at the distance of closest approach) are also given. If it is assumed that the dielectric constants of the various systems are approximately the same,[21] a reasonable assumption in *similar* systems, the ion-oxygen product is obviously proportional to

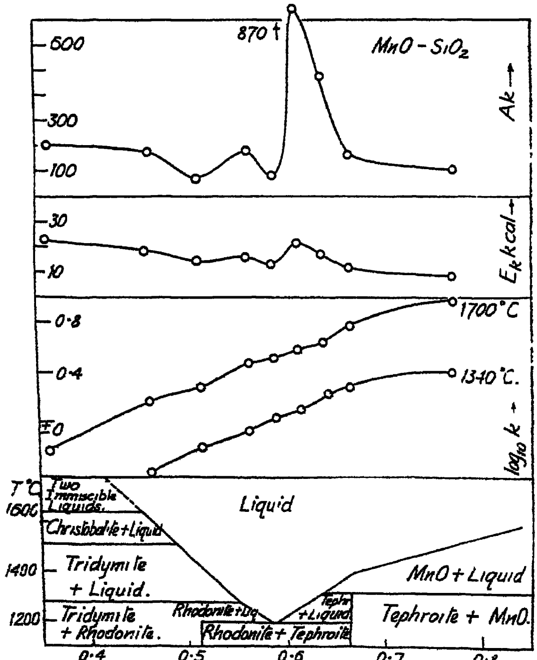

FIG. 3.

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[21] Eitel, *Physikalische Chemie der Silikate* (Leipzig, 1929), 115.

* The data on viscosity,[9] mainly for comparatively low temperatures, are very limited and particularly in need of extension.

† Even with these measurements, comparison is difficult because they were carried out at a much lower temperature than that of most of the present work. Thus the value at 1300° C. for the $CaO-SiO_2$ system given in Table II is extrapolated from the $\log_e \varkappa - \frac{1}{T}$ relation in the molten state.

the coulombic attraction between M^{2+} and O^{2-}. Of the five results, four are in the same order as their ion-oxygen products and the conductivity of the divalent systems is in both cases higher than that of the monovalent systems.

Discussion

(i) **General Mechanism of Conduction.**—Conductivities of the $CaO-SiO_2$ and $MnO-SiO_2$ melts have the same order of magnitude as those of typical ionic melts ($CaCl_2$ or KCl) extrapolated to the same temperature. This might be regarded as satisfactory proof of the ionic mechanism of the conduction process in the former systems. As the undissociated oxide structure is generally assumed [22] for these systems, however, some discussion of the evidence for their ionic constitution will be given.

Firstly, in a general way it is improbable on the grounds of the nature of CaO and MnO in the solid state that their melts would consist of "compounds," i.e., essentially undissociated entities of no net charge. CaO and MnO are ionic solids having the rock-salt structure, e.g., CaO has about 75 % "ionic character [23]" in comparison with about 80 % "ionic character" possessed by NaCl. Also, the colour of fused $MnO-SiO_2$ mixtures up to 60 % MnO is distinctly pink, thus indicating the presence of manganese ions.

TABLE III

CHANGE OF CONDUCTIVITY AT M.P. FOR TYPICAL ELECTROLYTIC AND ELECTRONIC CONDUCTION AND FOR SILICATE MELTS

System	$\frac{\varkappa\text{ (above m.p.)}}{\varkappa\text{ (below m.p.)}}$	Remarks
NaCl	3×10^3	Typical ionic melt
$CdCl_2$	2×10^2	Typical ionic melt
AgCl	3×10^1	Typical ionic melt
Hg	0·2	Typical electronic conductor
Pb	0·5	Typical electronic conductor
1/1 $CaO-SiO_2$	2×10^1	Ionic conduction
1/1 $MnO-SiO_2$	3×10^2	Ionic conduction
$Al_2O_3-SiO_2$ (0·08 mol. Al_2O_3)	1	Possibly ionic conduction

The principal facts directly in favour of a predominantly ionic conduction in the systems examined here may be summarised as follows:—

(1) Increase of conductivity with increasing temperature is expected for ionic, not electronic (metallic), conduction.[24] The energy of activation/mol. (E_k) is about 10–35 kcal. which is typical of the energy of activation for ionic conduction known from experiments on ionic solids.

(2) In the systems $MnO-SiO_2$ and $CaO-SiO_2$, the conductivity is of the order of $10^{-1}-10$ mhos over the composition examined and $10^{-4}-10^{-3}$ mhos for $Al_2O_3-SiO_2$. Conversely, molybdenum, a fair electronic conductor, has a conductivity of about 2×10^4 mhos at 1700° c. and the extrapolated (hypothetical) value for Bi, a bad electronic conductor, is about 4×10^8 mhos at 1700° c.

(3) The conductivity of the systems containing CaO and MnO increases regularly with increase of MO; this type of dependence on concentration is usually associated with ionic conductors.

(4) A characteristic of ionic conduction is a rapid decrease during the transition from liquid→solid; of electronic conduction a corresponding relatively small increase [25] (see Table III).

Thus, $CaO-SiO_2$ and $MnO-SiO_2$ have a ratio of the same order as ionic melts such as $CdCl_2$ in which ionic conduction has been conclusively proved. This ratio is also important as a measure of the imperfections in the lattice; the greater is the ratio, the more perfect the solid crystal tends to be.[26] This concept agrees well with the glassy nature of the Al_2O_3—SiO_2 system in the solid state.

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[22] Heinemann, *Bull. Acad. Sci. U.R.S.S.*, 1946, **10**, 1439.

[23] Wells, *Structural Inorganic Chemistry* (1945), 311.

[24] Hevesy, *Handbuch der Physik*, 1928, **13**, 270.

[25] *Idem.*, *ibid.*, 266.

The above facts are in agreement with the concept that the mechanism of conduction in the systems examined is ionic It might be suggested that the positive temperature coefficient of conduction and order of magnitude of the energy of activation could also be interpreted according to a semi-conduction mechanism, which is known to exist in certain metallic oxides.[27] There are, however, several lines of evidence which make the mechanism of semi-conduction seem unlikely for the present systems. Firstly, such a mechanism is essentially a "structure-sensitive" property, i.e., it depends largely upon mode of pre-treatment, particularly oxidation and reduction, which may cause changes in conductivity of several powers of 10 in true semi-conductors. The conductivity of the systems examined here was hardly affected, however, by the use of various gases as atmospheres. Further, there is no evidence to show that semi-conductors have a positive temperature coefficient in the high temperature ranges used here: the disorder of the lattice caused by increasing temperature tends to reduce the conduction when the temperature is raised and this tendency may overcome the increase of conductivity with rise of temperature which normally occurs in semi-conductors due to the release of more free electrons. The parallelism between fluidity and conductivity would also not be expected were semi-conduction to be important here. Again, the specific conductivity of solid CaO and Al_2O_3 is known at high temperatures,[28] and is of the order 10^{-3} and 10^{-4} mhos respectively at 1650° c. This is far too small to give rise to the conductivities observed here. The conductivity of solid MnO was examined by the present workers over the range 500°–1100° c. in a forming-gas atmosphere (which causes no reduction of MnO at these temperatures) The conductivity was found to be very considerable and to increase rapidly in the region 900°–1100° c., where it is about 10^4 times greater than that of CaO. It is hence very probable that MnO exhibits semi-conduction in the solid state. However, extrapolation of the conductivity to 1700° c. yielded a result of about 4×10^2 mhos/cm.^{3}, which is about 50 times *larger* than that observed on extrapolation of the results obtained from the melt to 100 % MnO.

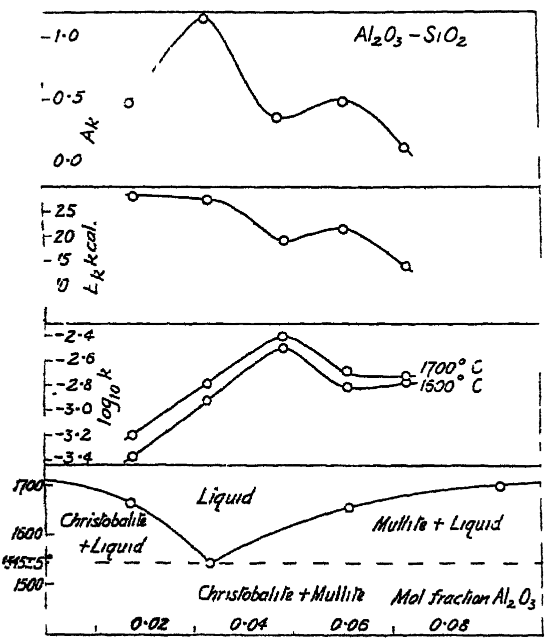

FIG. 4.

Against these strong reasons for the rejection of an appreciable component of electronic conduction in the silicate melts examined, it was observed that in melts containing a large molar fraction of manganous oxide (> 0·8) the ratio $\frac{\kappa \text{ (in liquid)}}{\kappa \text{ (in solid)}}$ at the m.p. is much less than that observed (10^2) for the other melts in this and the system containing CaO. This fact, taken alone, might indicate an appreciable component of semi-conduction in these high MnO contents. Were this to occur, however, a more rapid increase of $\varkappa$ with molar fraction of MnO in the range of high concentration of MnO might be expected, whereas the converse is observed. A quite unambiguous decision concerning the existence of semi-conduction in this concentration region of high MnO could only be obtained by examination of the Hall effect and the applicability of Faraday's laws of electrolysis.

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[26] Hevesy, *Handbuch der Physik*, 1928, **13**, 289.

[27] For review see Gudden, *Naturwiss.*, 1943, **13**, 223.

[28] Podszus, *Z. Elektrochem.*, 1933, **39**, 75.

It can, therefore, be concluded that the mechanism of conduction in the systems reported here is predominantly ionic. In those containing CaO and MnO, comparison with the conductivity of totally dissociated ionic melts under similar conditions suggests that a high degree of dissociation pertains in the melt and in that containing Al_2O_3 a low degree of dissociation. It is possible that some electronic semi-conduction occurs in the $MnO—SiO_2$ systems when the molar fraction of MnO exceeds 0·8.

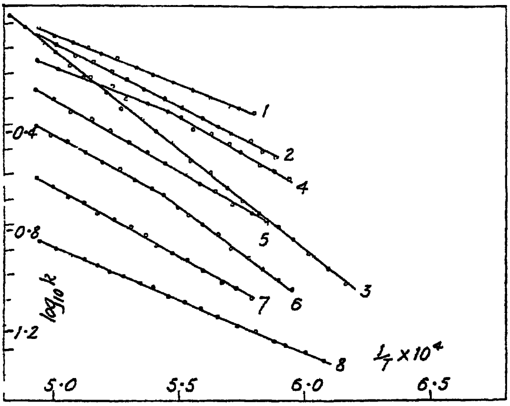

FIG. 5.—Dependence of conductivity of $CaO—SiO_2$ on temperature for various compositions :—
% CaO: 1, 55 %; 2, 50 %; 3, 60 %; 4, 45 %; 5 40 %; 6, 35 %; 7, 20 %; 8, 30 %.

(The term degree of dissociation is used here in a modern sense and implies no equilibrium between dissociated ions and undissociated molecules. Thus if α is the degree of dissociation, this means that a fraction α of cations and/or anions is relatively free to conduct, as opposed to being held under a coulombic or other field due to another entity, so strongly that relatively independent movement under an applied field cannot take place.)

(ii) Tentative Model of the Silicate Melts containing Metal Oxides.—To explain the high ionic conduction observed in the systems studied, two very general models could be employed. Either, the melt might consist of M^{z+} and O^{2-} ions and silica, or it might consist of M^{z+}, O^{2-} and silicate ions of various types. In the latter model, the concentration of free O^{2-} ions could be very small. The first model will be rejected on the following grounds. (i) The dielectric constant of the melt is probably about 3–6.[21] In such a medium, ionic association [29] between M^{z+} and O^{2-} would be very considerable and hence the conduction would be very small. (ii) The viscosity of such melts at low MnO content is large,[8] though it decreases considerably on the addition of MO; this would only be consonant with extensive coupling and complex formation decreased upon addition of MO among the silicate groups, which determine the viscosity. (iii) According to X-ray data,[9] silicate tetrahedra are present in solid silicates at high temperatures. Hence, their presence seems likely in the melts, which, in accordance with modern views on the structure of liquids, can be regarded as a disordered form of the solid.

The structure of silicates in the solid state is reasonably well known, largely through work of Warren [30] [9] and of Zachariasen.[31] In the liquid state, X-ray data [9] show diagrams which do not consist of sharp patterns, but indefinite rings, and this accords with the concept that the essential difference between the solid and molten silicate lies in the degree of order of the lattice, the liquid state being characterised by an extended network lacking symmetry and periodicity. The molten silicate can be regarded as consisting of a series of spatial, tetrahedrally-co-ordinated rings and chains, arranged in an irregular fashion. When a metal oxide is added to such a system, the metal ions must fit into the interstices of the structure. The reduction of viscosity caused by the addition of metal oxide suggests that this fitting into the silicate lattice causes extensive breakdown of the original highly co-ordinated lattice so that the original spatial co-ordination will be converted into large configurations, then into single chains and finally into silicate tetrahedra. This model has been recently used by Endell[32] and co-workers in a convincing interpretation of the effect of metal oxides on the viscosity of silicate melts.

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[29] Bjerrum, *Kgl. Danske Vid. Selk. Mat.-fys. Medd.*, 1926, 7, No. 9; Fuoss, *Chem. Rev.*, 1935, 17, 227.

[30] Warren, *J. Appl. Physics*, 1942, 13, 602; *Tech. Rev.*, 1942, 43, 253 and 273.

[31] Zachariasen, *J. Amer. Chem. Soc.*, 1932, 54, 3841.

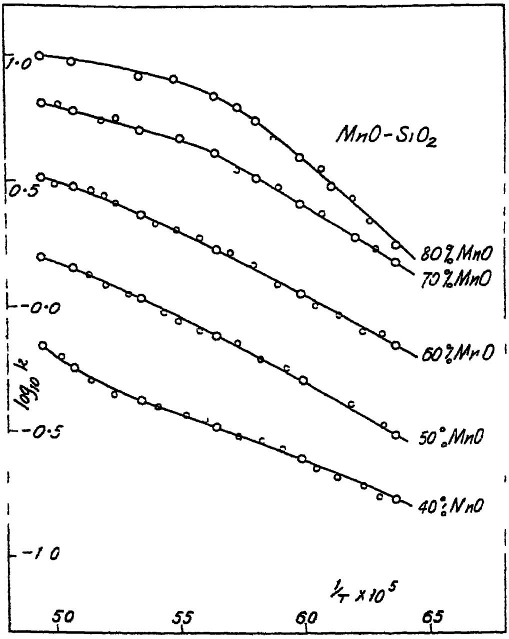

FIG. 6.—Dependence of conductivity of $MnO-SiO_2$ on temperature for various compositions.

In the following, it will be shown that a successful interpretation of the electrical conductivity of molten silicates can be obtained on the basis of this model. Thus, considering the cation M^{z+} this can be regarded as existing in an "energy well" in the interstices of the silicate structure, the height of the energy well being E_κ. The probability of the cation escaping from the well is proportional to $e^{-E_\kappa/RT}$ and E_κ will be reduced by the application of an applied potential, thus giving rise to preferential jumps by the cation in the direction of the applied field. Thus, in a general way, κ, the specific conductivity is given by :

$$\kappa = \text{const. } c\, e^{-E_\kappa/RT} \quad . \quad . \quad . \quad . \quad (1)$$

where c is of the order of the vibration frequency of M^{z+} in the interstices. Hence

$$\kappa = A\, e^{-E_\kappa/RT} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where A will be called the frequency factor, and E_κ the energy of activation. A contains also mobility and concentration terms.*

Eqn. (2) will be applicable to a binary system if (i) the energies of activation for transport of cation and anion are nearly equal or (ii) virtually only one ion conducts, i.e., if the E_κ value for one ion is much less than that for the others, so that the transport number for one ion is almost unity.†

[32] Endell and Kley, *Stahl Eisen*, 1939, **59**, 677.
[33] Rasch and Hinrichsen, *Z. Elektrochem.*, 1908, **14**, 41.

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* This equation is sometimes known as the Rasch-Hinrichsen law and was deduced empirically by these authors.[33]

† The equation $\lambda = A' e^{-E_\lambda/RT}$ also holds for the relation between the equivalent conductivities and temperature. It is often preferable to use this equation for comparison of the energies of activation of the migration of various salts because the conduction is then due to one equivalent of salt between electrodes at a distance apart of 1 cm. all the time. Its use is precluded in the present case because of the absence of sufficient density data in molten silicate systems.

Further, the variation of the viscosity of liquids with temperature is given by the equation :[34]

$$\eta = Be^{+E_\eta/RT} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

where E_η is the height of the energy barrier for viscous flow and B is a frequency factor.

(iii) **Detailed Application of Model.**—Some experimental values of E_κ, E_η, and A are given in Table IV. E_κ (see Fig. 5, 6 and 7) remains approximately constant with variation of temperature over the whole temperature range studied for $Al_2O_3-SiO_2$. For $MnO-SiO_2$ a change in E_κ with temperature is noticeable for 0·66 and 0·77 molar fraction MnO and this also occurs for 0·37–0·47 molar fraction CaO. It follows that for Al_2O_3 conduction is probably by one ion over the range examined. For $CaO-SiO_2$ and $MnO-SiO_2$, either more than one ion takes part in the migration, or else structural changes take place in the melt at temperature and composition mentioned above.

TABLE IV

ENERGY OF ACTIVATION FOR IONIC MIGRATION AND VISCOUS FLOW IN SILICATE MELTS

System	% MO or M_2O_3	A	E_η kcal./mol.	E kcal./mol.	Si/O Ratio
KCl	—	6·5	2·3	7·8	—
$CaCl_2$	—	13·5	4·1	9·5	—
$CaO-SiO_2$	20	148	26	—	0·441
,,	30	153	26	—	0·407
,,	35	164	24	—	0·388
,,	40	321	26	—	0·368
,,	45	1550	31	31	0·348
,,	50	247	23	34	0·325
,,	55	115	19	35	0·302
$MnO-SiO_2$	40	207	22	—	0·39
,,	50	180	18·6	—	0·35
,,	55	71	14·3	—	0·33
,,	60	176	15·7	—	0·30
,,	62·5	81	13	28	0·293
,,	65	870	21	—	0·28
,,	67·5	480	17·5	30 (67 %)	0·267
,,	70	160	11·5	54	0·25
,,	80	100	8	—	0·196
$Al_2O_3-SiO_2$	3	0·5	27	—	0·487
,,	5·5	1·2	26	—	0·476
,,	8	0·4	19	—	0·465
,,	10	0·5	22	—	0·455
,,	12	0·1	14	—	0·447

In the system $MnO-SiO_2$, these two possibilities can be distinguished by a comparison of E_κ and E_λ. E_η is approximately 2–4 times as large as E_κ. Hence, conductivity in this system involves transport across a different energy barrier to that of viscosity. The latter is known to be controlled by the large silicate ions [35] so that the former must be controlled by the small manganous ions. It is, therefore, probable that in this system conduction is entirely cationic, i.e., by reason of divalent manganese ions which pass through the silicate lattice. (cf., the analogous relations between E_κ and E_η for typical cationic conduction shown in Table IV for KCl or $CaCl_2$.)

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[34] Dunn, *Trans. Faraday Soc.*, 1926, **22**, 401 ; Andrade, *Phil. Mag.*, 1934, (7), **17**, 698 ; Eyring, *J. Chem. Physics*, 1936, **4**, 283 ; Ward, *Trans. Faraday Soc.*, 1937, **33**, 88 ; Barrer, *Trans. Faraday Soc.*, 1943, **39**, 48.

[35] Frenkel, *Acta Physicochim.*, 1937, **6**, 343.

A similar, but less certain, conclusion can be drawn from the $CaO-SiO_2$ system. The difference between E_κ and E_η is here less than that for $MnO-SiO_2$ and it is possible * that the formation of the ion complex $Ca^{-+}SiO_3^{-}$ interferes with the relation for the composition 45 % $CaO-SiO_2$.

The cationic conduction indicated here would not be wholly expected because with increase of temperature there is usually an increased tendency for anionic conduction to occur in ionic melts. The large radius, high degree of co-ordination and large polarisability of the silicate ion must prevent, or largely reduce this.

The relation between conductivity of various systems at the same temperature of comparable compositions and nature of the cation (see Table II) follows by a consideration of the coulombic interaction between M^{z-} and O^{2-}. Upon this latter factor clearly depends the amount by which the metal ion will disturb the structure of the silicate, for if the radius is small and the charge high the attraction for oxygen is large and a relatively considerable break-up of the structure ensues. Break-up of the silicate structure signifies an easier passage of the metal cations through the interstices of the melt and hence increases the conductivity. The results of Table II follow clearly from this with the exception of the anomalous result for K^+.

It is well known that the electrophilic properties of "acidity" of a charged group is a function of the field at its periphery. The larger the ion, the lower is the electric field at its surface and therefore the less its tendency to accept electrons. It follows from this that there should be a lowering of conductivity with increase of more "basic" components in the melt and this explains the general trend reported by Martin and Derge [18] from their examination of the $CaO-Al_2O_3-SiO_2$ system. Examination of Table II shows that a simple steric model, according to which the conductivity of the ions is in order of their ionic radii, does not alone suffice for an explanation of the dependence of conductivity on the nature of the cation.

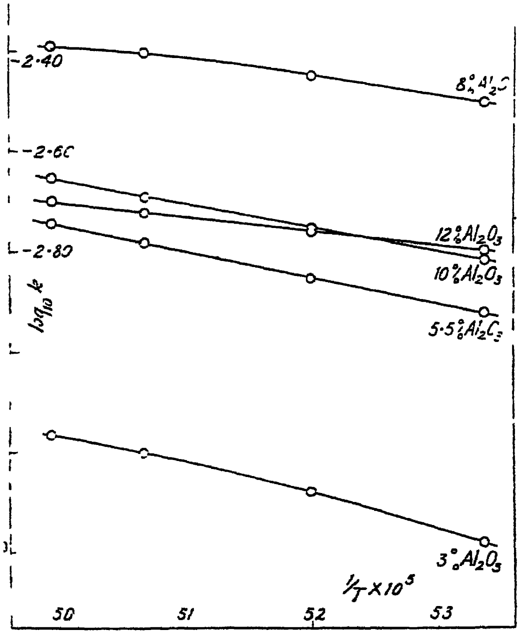

FIG. 7.—Dependence of conductivity of $Al_2O_3-SiO_2$ on temperature for various compositions.

The radically different behaviour of the $Al_2O_3-SiO_2$ system also becomes a consequence of the present model. For ions, the ionic potential of which is relatively small, decrease of radius on increase of valency merely has the effect of attracting some of the oxygen ions held in the silicate tetrahedra and thus breaking down the structure. When the ionic potential becomes relatively large, however, so that the ion oxygen attraction of the metal ion is comparable to that of Si^{4+}, the metal ion itself commences to form a lattice in which it is relatively immobile. The ion oxygen attraction of Al^{+++} is 1·7 approximately

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* Although ionic migration and viscous flow are probably governed by energy barriers of different magnitudes in these systems, there may still be a parallelism between conductivity and fluidity (as observed here) because the quantities may both be (different) functions of the same structural changes in the melt.

(cf., 0·27 for K^+, 3·1 for Si^{4+}) and hence a greatly increased tendency for complex anion formation occurs for Al^{+++} compared with K^+ or Ca^{++}. Crystallographically, it is known that Al^{+++} can form AlO_4^{-----} ions corresponding to SiO_4^{----} ions. Hence, small concentrations of Al_2O_3 doubtless produce an appreciable concentration of semi-mobile Al^{3+} ions, so that the conductivity of the Al_2O_3—SiO_2 melt at first increases with increase of Al_2O_3 concentration. At a given concentration, the anion-forming properties begin to predominate, the increased viscosity thus giving rise to a decreased conduction.

A matter of considerable interest is that of the possible existence of so-called compounds in the melt, a view which is frequently put forward in the metallurgical literature[3, 4] If by "compound" is meant a substance whose constituent atoms are not held together by primarily ionic bonds, this view seems to lack meaning in the systems examined here, particularly the systems containing CaO and MnO, where the concept of definite molecular entities in a melt produced from the ionic solid is an *ad hoc* assumption with no direct supporting evidence. The problem of estimating accurately the degree of dissociation is one which has not been solved electrochemically: it is, therefore, not possible to deduce quantitatively any figure for the degree of dissociation in melts containing CaO and MnO. It must be a high degree, however, as shown by the comparison with completely dissociated melts in Table I. The comparatively high conductivity may be due in fact to higher mobilities of Ca^{++} and Mn^{++} in comparison with those of, for example, K^+ or Cd^{++} in melts of their chlorides, but the higher viscosity of the silicate melts somewhat negates this consideration and the difference in mobilities of these ions in media of the same resistance would be small. The proportion of free ions in the Al_2O_3—SiO_2 melts of, say, 0·05 molar fraction Al_2O_3 must be of the order of 10^{-3} less than that in the other two systems.

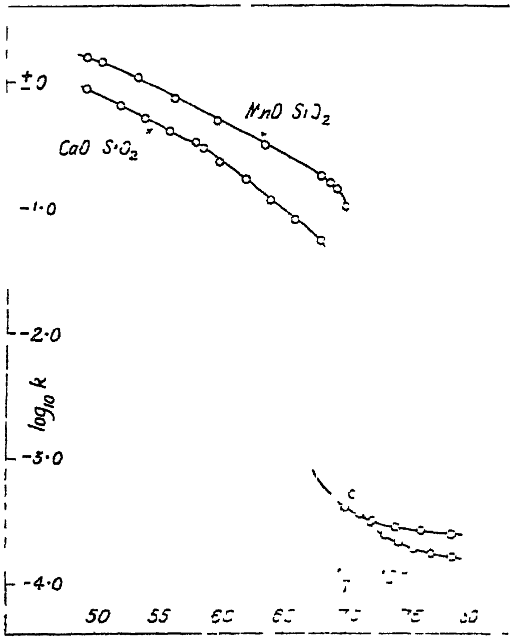

FIG. 8—Typical relation of conductivity and temperature (1750°–1000° C.).

Heinemann,[22] from an analysis of the thermodynamic data on slag-metal equilibrium, concluded that although FeO and some other entities were fully dissociated in their silicate melts, CaO formed some proportion of the complex $Ca^{++}SiO_3^{--}$ in fayalite. Examination of the present data for a similar association in the systems containing CaO and MnO can first be made from the conductivity isotherm. When a complex or compound exists in the melt, this is usually indicated by a minimum on the conductivity isotherm; it is sometimes found that the latter exhibits a minimum at a temperature near that of the melting point of the "compound" and that this disappears on raising the temperature.[26] It is seen from Fig 2 and 3 that no significant minima are found on the conductivity isotherms.

It is, however, of interest that maxima occur on the relations for E_κ and A

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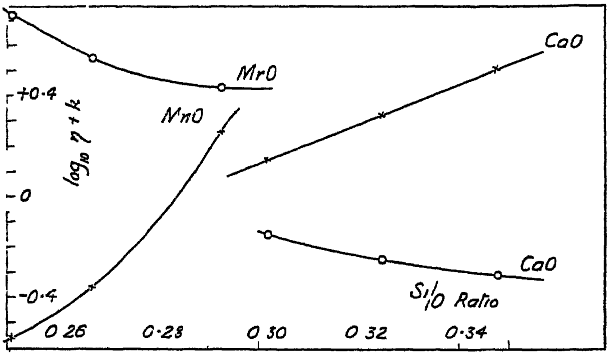
[26] Babcock, *J. Amer. Ceram. Soc.*, 1934, **17**, 329.

in the region of the compound tephroite (2 $MnO-SiO_2$) in the $MnO-SiO_2$ system and calcium meta-silicate in the $CaO-SiO_2$ system. An explanation of this result may be realised when it is recalled that E_K, calculated from a plot of $\log_e \varkappa$ against $\frac{1}{T}$, is actually a heat of activation, and that an entropy term $e^{\Delta S/R}$ must be included in the A factor. At compositions corresponding to greater order, namely in the region of the stoichiometric relations, ΔS would be expected to increase and this is manifested by the increase in A.

If the tendency towards ion association is very great, then the increase in E_K overcomes this corresponding increase in A so that a reduction in conductivity, and hence a minimum on the conductivity isotherm, may occur.

It can therefore be concluded that in the $CaO-SiO_2$ and $MnO-SiO_2$ systems, no evidence for general *substantial* complex formation, or the formation of "compounds" exists. There is some evidence for a tendency towards complex formation in regions corresponding to the complexes Ca^{-+} SiO_3^{--} and $(Mn^{++})_2$ SiO_4^{----}.



× $\log_{10}\eta$ ○ $\log_{10}\varkappa$

FIG. 9.—Relation between conductivity and viscosity at 1600° c. as a function of Si/O ratio.

Comparison of the energy of activation with the Si/O ratio for various systems at the same temperature shows a decrease with decreasing Si/O ratio. The decrease of the activation energy is associated with the increased formation of single silicate tetrahedra and hence with the breaking-down of the silicate structure, so that the conductivity increases.

The present model also gives understanding of the hysteresis phenomena which occur on heating and cooling. It would be expected on general energetic grounds that the interstitial ions would tend to take up the most stable position in the deepest energy wells. On cooling, these ions will tend to return to their most stable, and thus least conducting, positions. If, however, cooling is carried our fairly rapidly, the cations have insufficient opportunity to return to their deepest energy levels and the system possesses still a comparatively high conduction at temperatures below the melting point. When measurements are repeated during the heating-up process, more time has elapsed in which the ions may assume deeper energy levels and the conduction is hence decreased. At temperatures above the true m.p., when the system has considerable fluidity, measurements taking in ascending and descending directions coincide within the experimental error.

Experimental work on the constitution of the silicate melts is being pursued further in this department.

Thanks are due to Dr. H. Bloom, Dr. F. D. Richardson, and Dr. J. White and to Mr. J. H. E. Jeffes for helpful comments on the paper; and to the British Iron and Steel Research Association for the financial support of this work, including bursaries to two of us (S.I. and J.W.T.).

Summary

The electrical conductivity of the systems CaO—SiO$_2$ (mol. fraction CaO : 0·27—0·60), MnO—SiO$_2$ (mol. fraction MnO : 0·35–0·77) and Al$_2$O$_3$—SiO$_2$ (mol. fraction Al$_2$O$_3$: 0·01—0·08) has been determined over the temperature range 1000°–1800° C. The results down to the temperature of " apparent solidification " are reported here.

In the systems CaO—SiO$_2$ and MnO—SiO$_2$, the conductivity increases regularly with increase of the metal oxide ; in the system Al$_2$O$_3$—SiO$_2$, the conductivity passes through a maximum at a concentration of about 0·05 mol. fraction Al$_2$O$_3$. The systems in the molten state obey the Rasch-Hinrichsen law well. The energy of activation varies over the approximate range 10–35 kcal. for various systems.

The conduction in all systems is primarily ionic, and probably mainly cationic. A semi-conduction mechanism may also be operative at high MnO contents in the MnO—SiO$_2$ system.

In the CaO—SiO$_2$ and MnO—SiO$_2$ systems, the degree of dissociation into ions is substantial ; in the Al$_2$O$_3$—SiO$_2$ system it is small, and extensive association occurs. It is improbable that any compounds exist in the melt as molecular entities corresponding to the conventional formulæ. It is probable that complex formation is increased in the melt in a composition range corresponding to the ion pairs Ca^{++} SiO$_3^{--}$ and (Mn^{++})$_2$ SiO$_4^{----}$.

The dependence of conductivity on temperature is complex in the neighbourhood of the melting points according to phase diagrams. A conductivity hysteresis with temperature exists during measurements with increasing, as compared with decreasing, temperature, at temperatures below the m.p.

The conductivity in the systems CaO—SiO$_2$ and MnO—SiO$_2$ varies with composition in a way roughly parallel to their fluidity.

A model for the conduction mechanism is described and shown to result in a satisfactory interpretation of the principal observations. There is some experimental support for the deduction that the conductivity at the same temperature and mol. fraction of metal oxide decreases in order of decreasing coulombic interaction between the metal cation and the oxygen ion at the distance of closest approach.

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THE CONSTITUTION OF PHASES AT HIGH TEMPERATURE IN RELATION TO THEIR THERMODYNAMIC PROPERTIES

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In spite of the common use of the methods of chemical thermodynamics in the study of metallurgical reactions at high temperatures, the literature does not contain any explicit account of the limitations of these methods in this field. It is the aim of this account to draw attention to those difficulties in the use of the usual thermodynamic methods which are of particular importance in the metallurgical field.

The usual method of calculating high temperature equilibria from data such as heats of formation, entropies, heat capacities, etc., is based on the assumption that definite values for all the thermodynamic properties may be obtained for all chemical substances. This is true for compounds only if the compound obeys the law of constant composition, i.e., is strictly stoichiometric. For gases and organic molecules the molecular constitution does not permit of any variability in composition ; on the other hand, the requirement of electrical neutrality which for ionic compounds is generally sufficient to ensure constancy of composition, may not always do so.

Many inorganic compounds do not obey the law of constant composition, and may be stable over a range of composition, which may not include the stoichiometric compound. Since the production of the lattice defects which are responsible for the variation in composition requires energy, such variability in composition is greatly favoured by high temperatures and has been found for a wide range of oxides, sulphides, etc.[1] For any non-stoichiometric compound the thermodynamic properties must be given as functions of its composition.

The relation between oxygen (or sulphur) pressure and composition of the solid oxide (or sulphide) is the most widely studied equilibrium property of non-stoichiometric compounds. In qualitative agreement with theory,[2] the equilibrium partial pressures vary considerably with composition. The order of magnitude of the effect may be illustrated by the results of Darken and Gurry [3] for wüstite, where the partial pressure of oxygen increases by a factor of the order of 10^3 for an increase in atomic ratio O/Fe from about 1·05 to 1·2. Such variations in, e.g., oxygen pressure with composition are of considerable importance in heterogeneous equilibria, for which one of the equilibrium conditions is that the oxygen pressures of all phases must be equal. From partial pressure against composition curves at constant temperature, the activity of the metal may be obtained by the Gibbs-Duhem equation relative to some arbitrary standard state, such as a definite composition of the compound, or the compound in equilibrium with another phase, such as the pure metal.

For the compound AB, the activities of A and B are related by the Gibbs-Duhem equation,

$$\log a_A = -\frac{N_B}{N_A} \log a_B$$

where the a's are activities. The activity of the compound AB may be defined in terms of an arbitrary standard state by $a_{AB} = a_A a_B$ and will also vary with composition, since a_A is not proportional to $1/a_B$. It follows that saturation of a slag, say, with an oxide does not mean that the activity of the oxide in the slag is constant, unless it is of constant composition, independent of the slag composition.

In spite of the marked variations of activities with composition, the free energy of formation of a total of 1 mole of (A + B) probably does not vary greatly with composition. There are no direct experimental determinations in the literature but from a consideration of free energy against mole fraction curves, in general, little change in free energy with composition is required to produce large changes in the partial molar free energies of the elements, which are given by the intercepts of the tangent to the free energy against mole fraction curve on the ordinates $N_A = 0$ and $N_B = 0$. It seems probable that the variations of free energy with composition are generally comparable with the uncertainty due to experimental errors in the thermal data. If required, the free energy of formation G per mole (A + B) can be obtained from the partial molar free energies $\bar{G}_A$ and $\bar{G}_B$ using the relation

$$G = \bar{G}_A N_A + \bar{G}_B N_B.$$

Since the composition of a non-stoichiometric compound is dependent on both temperature and the partial pressure of one of the components, any such compound must be regarded as a two component system, where the classical compound of fixed composition represents only one component. In equilibria involving variability of composition of a compound, an extra degree of freedom is introduced, above those which would be found when the compound is counted as a single component. Thus, the melting at constant composition of such a phase takes place over a range of temperature, i.e., both solidus and liquidus lines have to be determined. Only when solid and liquid phases have the same composition at the same temperature (i.e., maximum or minimum melting points) will melting take place at constant temperature. Unless melting is carried out at constant composition of the solid, with the gas in equilibrium throughout, results may be considerably in error. Considerations such as these probably account for part of the discrepancies in the literature for many melting points such as those of sulphides. Similar remarks probably apply to the volatilisation of a compound where the partial pressure of the compound in the gas phase will depend on the composition of the solid, and hence on the composition of the gas. In general, the equilibrium properties are not to be regarded as those of a definite chemical species, but as those of a range of substances which form a single phase.

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[1] Anderson, *Ann. Reports*, 1946, **42**, 104.
[2] Wagner and Schottky, *Z. physik. Chem. B*, 1930, **11**, 163.
[3] Darken and Gurry, *J. Amer. Chem. Soc.*, 1945, **67**, 1398.

Many liquids, including slags, may be regarded as being derived from the more widely studied solid non-stoichiometric compounds. The excess oxygen (and ferric iron) found in wüstite in equilibrium with metallic iron is also found in the following liquids in equilibrium with metallic iron: liquid iron oxide,[4] and slags containing in addition SiO_2,[5] $CaO + SiO_2$,[6] $M_5O + SiO_2$,[7] and acid and basic steel-making slags. These may be regarded as derivatives of the oxygen-rich wüstite phase. Antimony in the system $PbO\text{-}Sb_2O_3$ apparently is similar to iron in basic open-hearth slags in acting as an " oxygen-carrier," as shown by its accelerating effect on the rate of oxidation of lead bullion.[8] The liquid dross apparently is capable of combining with more oxygen than corresponds to Sb_2O_3; the observations of Maier and Hincke [9] on the production of a higher oxide are in agreement with this view, and the observed disproportionation is in agreement with the theory which has been developed for binary systems by Anderson.[1]

In many systems containing liquid sulphides in equilibrium with a metal phase, the sulphide contains less than the stoichiometric amount of sulphur. A similar deficiency in sulphur is found in copper and nickel mattes but may be partly due to the replacement of sulphur by oxygen.[10] Since a deficiency of sulphur is not common in the corresponding solid sulphides, it is possible that the changes on melting here are more fundamental than those in oxide systems, and are due to the greater extent of covalent bonding in sulphides.[11]

The systems to be used in a statistical treatment of the relation between composition and thermodynamic properties of solid non-stoichiometric phases are the atoms of the elements, since it is the distribution of these over the lattice sites which is responsible for the possibility of variation in composition. Any attempt to treat wüstite, say, as a solid solution of Fe_2O_3 in FeO is bound to be unsuccessful, since such a treatment, in terms of the ordinary solution laws must imply a distribution of discrete FeO and Fe_2O_3 molecules or similar molecular species over a set of sites available for molecules of both types. Since solid metal oxide phases are generally ionic and not molecular, the solution laws cannot be expected to apply. If the liquid phase is to be considered as a disordered structure related to that of the solid, similar considerations will apply, and as Darken and Gurry pointed out, the concept of a solution, which " presupposes the existence of molecular species " was not satisfactory in explaining their results for the liquid iron oxides.

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[4] Darken and Gurry, *J. Amer. Chem. Soc.*, 1946, **68**, 798.

[5] Bowen and Schairer, *Amer. J. Sci.*, 1932, **24**, 200.

[6] Bowen, Schairer and Posnjak, *Amer. J. Sci.*, 1933, **2**, 6222.

[7] Bowen and Schairer, *Amer. J. Sci.*, 1935, **29** 159.

[8] Williams, *Trans. Amer. Inst. Min. Met. Eng.*, 1936, **121**, 226.

[9] Maier and Hincke, *Trans. Amer. Inst. Min. Met. Eng.*, 1932, **102**, 97.

[10] Drummond, *Trans. Can. Inst. Min. Met.*, 1940, **43**, 627.

[11] Wells, *Structural Inorganic Chemistry* (Oxford, 1945), pp. 308, 385, *et seq.*

The concept of molecular species is not only inadequate for non-stoichiometric phases, but also in the application of the law of mass action to the distribution of metals between metal and non-metallic phases, such as the slag-metal equilibria of steel-making. Although the use of the law is admitted to be empirical by some writers, the limitations in its application do not appear to be widely recognised.

The literature contains many attempts to obtain information as to the constitution of slags from slag-metal equilibria. The usual procedure is to assume various compounds to be formed between the oxide components of the slag and, by trial and error, adjust these assumed combinations so that an equilibrium constant for the reaction can be obtained, using Raoult's law to relate activities to the mole fractions calculated from the assumed molecular species.

There are a number of objections to this method. Firstly, thermodynamics as such is not concerned with the constitution of matter, and thermodynamics alone cannot be used to determine the constitution of the system. Some relation between composition and the thermodynamic properties is required.

A further objection to the method of assuming likely molecular species and Raoult's law, is that the constitution so obtained is not necessarily unique. By the use of sufficient adjustable constants (including the formulæ of the assumed molecular species) it is probably always possible to obtain some sort of fit. Different workers have commonly obtained different results as to constitution by using different molecular species, and different solution laws. Thus, for the equilibrium between O_2 and molten iron oxides, White [12] assumed the molecular species in the melt to be FeO, Fe_2O_3 and Fe_3O_4, and the solution to obey Raoult's law ; Kielland [13] assumes a regular solution of FeO and Fe_2O_3 to describe the results of Krings and Schackmann,[14] while Darken and Gurry find both these unsatisfactory, and reject the treatment in terms of a solution of molecular species. Herasymenko [15] has shown it is possible to treat acid slags as ionic melts, in contrast to the more usual assumptions of a melt of oxides and silicates of Fe, Mn, etc. The distribution of phosphorus between basic slags and steel is described using Raoult's law by both Winkler and Chipman,[16] and by Balajiva, Quarrell and Vajragupta,[17] but with very different assumptions as to the predominant molecular species. The former assume $(2CaO.SiO_2)_2$ and $4CaO.P_2O_5$ with CaO, MnO and MgO equivalent to one another ; the latter assume $2CaO.SiO_2$ and $3CaO.P_2O_5$ with MgO and MnO not equivalent to CaO. Although due weight must be given to differences in experimental errors, it is clear that the conclusions as to constitution are not consistent, and from a purely empirical point of view, the method is unsatisfactory.

More important reasons may be advanced against this method of use of the law of mass action. Firstly, there seems to be no reason why molecular species should be assumed when discrete molecules do not exist in the solids concerned. Even if relatively stable ionic aggregates are assumed, on general grounds it is unlikely that such highly polar complexes would form ideal solutions.

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[12] White, *J Iron Steel Inst., Carnegie Mem.*, 1938, **27**, 1.

[13] Kielland, *Z. Elektrochem.*, 1935, **41**, 834.

[14] Krings and Schackmann, *Z. Elektrochem.*, 1935, **41**, 479.

[15] Herasymenko, *Trans. Faraday Soc.*, 1936, **34**, 1245.

[16] Winkler and Chipman, *Trans. Amer. Inst. Min. Met. Eng.*, Tech. Publ., No. 1987; *Met. Tech.*, April, 1946.

[17] Balajiva, Quarrell and Vajragupta, *J. Iron Steel Inst.*, 1946, **153**, 115.

The form which the mass-action expression takes in certain cases depends on the way in which the reaction is formulated. This was pointed out by Wagner[18] for the melt of $CdBr_2 + CdCl_2$. Schütza's[19] results for the equilibrium $CdCl_2 + Br_2 \rightleftharpoons CdBr_2 + Cl_2$ show the melt is not ideal if the usual mass-action expression is used. Wagner states that it should be formulated as $(Cl^-) + \frac{1}{2}Br_2 = (Br^-) + \frac{1}{2}Cl_2$ and is then ideal. The difference between the two formulations is that the first assumes independent molecular species of $CdBr_2$ and $CdCl_2$, while the second assumes only the anions to be concerned in the distribution. The concept of the ideal ionic solution introduced by Temkin[20] is an attempt to treat ionic melts in terms of the appropriate systems, viz., the ions. In general, where there is a difference in valency for the metal concerned, the ideal limiting law (i.e., assuming Henry's law for the dilute solute in both metal and non-metallic phases), is different according to whether the formulation is in terms of molecules or ions. Inspection of the alternatives, for example,

$$Ag_2O + Pb = PbO + 2Ag$$
$$2Ag^+ + Pb = Pb^{++} + 2Ag$$

shows that the limiting laws are not identical.

A similar problem is met with in distribution of phosphorus between steel and basic slags. The reaction is usually written as

$$2\,[P] + 5\,[FeO] + 3\,[CaO] \rightleftharpoons [(3CaO\,.\,P_2O_5)] + 5\,[Fe] \quad . \quad (1)$$

and the equilibrium constant is

$$K = \frac{[(3CaO\,.\,P_2O_5)]\ \ [Fe]^5}{[P]^2\,[FeO]^5\,[CaO]^3} \quad . \quad . \quad . \quad (2)$$

However, there is no reason for assuming that the dualistic empirical formula for the phosphate represents a molecular species. From the structures of the ortho-phosphates, the existence of discrete $PO_4^{\equiv}$ ions, analogous to $SiO_4^{====}$ appears likely,[21] and on this basis, the reaction may be written as

$$2\,[P] + 5\,[Fe^{++}] + 8\,[O^=] \rightleftharpoons 2\,[PO_4^{\equiv}] + 5\,[Fe] \quad . \quad . \quad (3)$$

$$\text{and } K' = \frac{[PO_4^{\equiv}]^2\,[Fe]^5}{[P]^2\,[Fe^{++}]^5\,[O^=]^8} \quad . \quad . \quad . \quad (4)$$

In the limiting case of very small phosphate content, and slag of constant composition, for which the activities of all the other reactants remain substantially constant and independent of $[PO_4^{\equiv}]$ one obtains from (2) assuming Henry's law to hold, that

$$\frac{[(3CaO\,.\,P_2O_5)]}{[P]^2} = \text{constant}$$

while (4) leads to $[PO_4^{\equiv}]\,/\,[P] = \text{constant}$. Although most of the results in the literature do not extend to very low P contents because of the analytical difficulties, it is significant that the P distribution ratio $[P_2O_5]\,/\,[P]$ has been often used as a means of classifying experimental results in terms of slag composition.[22]

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[18] Wagner, *Handbuch der Metallphysik Akademische Verlagsgesellschaft* (Leipzig, 1940), Vol I, Pt. 2, p. 103.

[19] Schutza, *Z. anorg Chem.*, 1938, **239**, 245

[20] Temkin, *Acta Physicochim.*, 1945, **20**, 411.

[21] Wells, ref. 11, p. 418

[22] A number of these distribution formulæ have been tested by Zea, *J. Iron Steel Inst.*, 1945, **151**, 459. The term [P] and not $[P]^2$ in Schenck's formula is to be noted.

It may be noted that even if some specific combination between Ca^{++} and $PO_4^{\equiv}$ is assumed, as seems necessary to explain the marked influence of lime in dephosphorising steel, then as long as the reaction product is monatomic with respect to phosphorus, the limiting law should be identical with that for (4).

The above discussion has assumed, of necessity, the validity of Henry's law as a limiting law. The wider question as to the type of solution law which is to be regarded as ideal for slags is not answered in the general case by the use of assumptions such as those made by Tempkin; since the mixing of ions of different valency cannot be completely random, because of the difference in electrostatic forces, and hence in energy which would follow an exchange of, say A^- for B^{--}. Further, even with a common cation the replacement is not 1 of A for 1 of B, but 2 of A^- for 1 of B^{--}, which must lead to a general change in structure. The requirements for random mixing *may* be met by similar ions, of the same charge and comparable ionic radius, but probably not by ions of different valency, as Wagner has pointed out in his discussion of the solution laws of molten salts.[23]

A molecular constitution for basic slags, giving a solution obeying Raoult's law implies the existence of definite molecular species, distributed at random through the liquid, which must be obtainable by mixing the liquid components without any heat effect or volume change. If this constitution is to be avoided, while maintaining the use of Raoult's law, some alternative model which when treated statistically will lead to the same law, must be devised. Failing a suitable model which can be treated by the methods of statistical mechanics to give the necessary relation between constitution and thermodynamic properties, the use of Raoult's law is best taken to represent an empirical method of simplifying the behaviour of multi-component systems.

As alternatives to the usual mass-action expression, two possibilities may be considered. One is the use of partial molar free energies for the equilibrium conditions. The other is to use alternative concentration scales, such as Tempkin's ionic fractions. The former approach is equivalent to an alternative to a logarithmic scale; the second gives rise to terms which are not greatly different to many expressions used for expressing basicity. Such methods, however, must remain empirical, since the necessary detailed knowledge which is required to determine the form of "ideal" laws is not available.

Summary

The concept of molecular species is examined in relation to the properties of non-stoichiometric phases, and in relation to the use of the law of mass action in steel-making equilibria. This law may take different forms, depending on whether the reaction is formulated in terms of molecules or ions. The validity of Raoult's law for basic slags is examined with reference to its implications as to the constitution of slags.

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[23] Wagner, *loc. cit.*, p 102.

EQUILIBRIUM RELATIONSHIPS IN SYSTEMS CONTAINING IRON OXIDE AND THEIR BEARING ON THE PROBLEM OF THE CONSTITUTION OF LIQUID OPEN HEARTH-SLAGS

By P. Murray and J. White

Received 25th *June*, 1948

It has long been known that equilibrium relationships between slag and metal in the open-hearth furnace can be represented by equilibrium constants of a mass-action form. Normally, for want of knowledge of the activity coefficients, such slag-metal constants have been expressed in terms of total concentrations of the reactants in slag and metal (weight or molar fractions in the slag and weight fractions in the metal) and, as has been pointed out,[1 2] such constants can only be considered true mass-action constants if no compounds are formed between the reactants in either of the liquid phases. This condition would appear to be fulfilled in the simple metal-metallic oxide system

$$(\mathrm{MnO}) + [\mathrm{Fe}] = (\mathrm{FeO}) + [\mathrm{Mn}]$$

and both the equilibrium constant,

$$K_{\mathrm{Mn}} = \frac{(\mathrm{FeO})\,[\mathrm{Mn}]}{(\mathrm{MnO})}$$

and the partition coefficient of FeO between slag and metal,

$$L_{\mathrm{FeO}} = \frac{[\mathrm{O}]}{(\mathrm{FeO})}$$

are found to be true constants,[3 4] independent of the ratio FeO/MnO in the slag and of the presence of inert diluents such as MgO.[5] (Here, as usual, round brackets indicate concentrations in the slag and square brackets concentrations in the metal, and the activity of metallic iron is taken as unity as its concentration over the usual range of compositions approaches 100 %.)

When silica is added to such a slag, however, K_{Mn} and L_{FeO}, expressed in terms of total concentrations in the slag, decrease in value, rather rapidly at first and then more gradually once the metasilicate composition has been exceeded.[6 7 8] Formally such effects can be attributed to a lowering of the activity coefficients of the FeO and MnO in the slag in the presence of silica,[9] the fall in K_{Mn} being accounted for, if the lowering for MnO is greater than that for FeO. Somewhat surprisingly, however, as shown by Körber and Oelsen,[8] these lower values of K_{Mn} and L_{FeO} in silica-saturated slags are, within narrow limits, independent of the ratio of MnO to FeO in the slag.

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[1] White, *J. Iron Steel Inst., Carnegie Mem.*, 1938, **27**, 1.

[2] White, *J Iron Steel Inst*, 1943, **2**, 579

[3] Körber and Oelsen, *Mitt. Kaiser-Wilhelm Inst. Eisenforsch*, 1932, **14**, 181.

[4] Korber, *Stahl Eisen*, 1932, **52**, 135.

[5] Krings and Schackmann, *Z anorg. Chem*, 1931, **202**, 337.

[6] Krings and Schackmann, *Z. anorg Chem.*, 1932, **206**, 337.

[7] Korber, *Z. Elektrochem*, 1937, **43**, 457.

[8] Körber and Oelsen, *Mitt. Kaiser-Wilhelm Inst. Eisenforsch.*, 1933, **5**, 271.

[9] McCance, *Iron Steel Inst.*, 1938, Special Report No. 22, 331.

The need for a simple comprehensive theory to account quantitatively for the effect of slag constitution on the activities of the components has long been felt. So far treatments based on two entirely different conceptions of the constitution of liquid slags have been attempted. According to one view, compounds which undergo partial dissociation into their component oxides occur in liquid slags, the degree of dissociation being governed by mass-action dissociation constants. In simple FeO–MnO slags, all the oxides are " free " and the measured constants are true mass-action constants. In more complex slags the various oxides are considered as partly " free " and partly combined, the activity of any oxide being measured by its " free " concentration. This is essentially the method adopted by Schenck,[10] by Chipman,[11 12] and by one of the present authors,[1] and this work has shown that good agreement with experimental and furnace data can be obtained. In direct contrast, Herasymenko [13] has assumed that the slag is completely dissociated into ions, thus accounting for the constancy of K_{Mn} in silica-saturated slags. From a consideration of the electrochemical potential existing between slag and metal at equilibrium, he shows that the constancy of K_{Mn} follows from the fact that it is numerically equal to the electro-chemical activity of iron in the metal layer. The change of K_{Mn} with basicity, he attributes to the presence of free oxygen ions in basic slags, this resulting in the formation of ions of the type FeO_2'' so that K_{Mn}, expressed in terms of the total concentration of iron in the slag, increases in value.

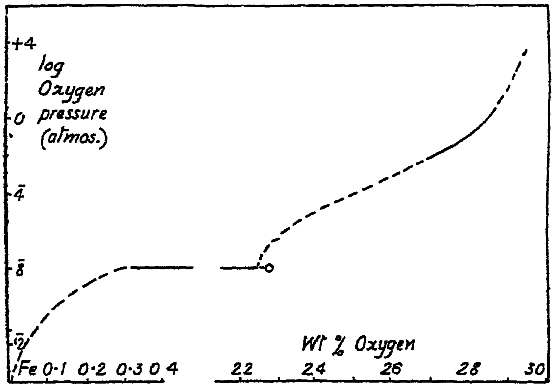

Fig. 1.—Oxygen-pressure-composition isotherm for melts of system FeO at 1592° c. Calculated curve for oxide phase shown dashed; experimental curve continuous ʘ limiting oxide composition according to Fetters and Chipman.[15]

More recently Lo Ching Chang and Derge[14] have used electromotive force measurements on a suitable cell to determine the activity of silica in CaO–SiO_2 and CaO–Al_2O_3–SiO_2 slags. As shown later (Fig. 5), the relation between silica activity in CaO–SiO_2 slags and composition as predicted by the present work is essentially similar to that actually found by them.

Of the two approaches, the electrochemical would appear the more likely to prove acceptable in the long run. It is, in fact, difficult to reconcile the conception of compounds dissociating into their component oxides in the liquid state with the known structures of oxides and silicate glasses, yet in spite of this the earlier work seems to show that treatments based on this conception lead to substantially correct predictions as far as the activities of the slag constituents towards the metal are concerned. The purpose of the present paper has been to re-examine the implication of this on a rather wider basis than has been previously attempted. The authors wish to emphasise, however, that they regard the assumption of compounds dissociating into oxides as a purely formal one and they do not consider that such compounds or free oxides necessarily exist as such in the liquid slag.

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[10] Schenck, *Introduction to Physical Chemistry of Steelmaking* (Translated by H. J. Goldschmidt, British Iron and Steel Research Assoc., 1945).
[11] Taylor and Chipman, *Trans. Amer. Inst. Min. Met. Eng.*, 1943, **154**, 228.
[12] Winkler and Chipman, *Met. Tech.*, 1946, **13**, No. 1987.
[13] Herasymenko, *Trans. Faraday Soc.*, 1938, **34**, 1245; *J. Iron Steel Inst.*, 1939, **1**, 282.
[14] Lo Ching Chang and Derge, *Trans. Amer. Inst. Min. Met. Eng.*, 1946, No. 2101.
[15] Chipman, *Trans. Amer. Soc. Met.*, 1942, **30**, 817.

Evaluation of Dissociation Constants in the Slag

Excluding electrochemical methods, there are three general ways in which information regarding the activity of a solute in a liquid phase can be obtained, these being by determining (1) its vapour pressure, (2) its concentration at saturation, i.e., at equilibrium with its pure, or nearly pure, solid phase, or (3) its concentration in a second immiscible liquid phase at equilibrium. In the case of liquid slags, data of the first kind are provided by slag-metal equilibrium data, e.g., the concentration of FeO or oxygen in the metal at equilibrium is a measure of the activity of FeO in the slag. Data of the first kind are not, at present, available and would probably be difficult to obtain, but in the case of the iron-oxide content of the slag somewhat analogous information, though more difficult to interpret, is provided by oxygen dissociation-pressure data on the liquid slag as shown by one of the present authors.[1] Activities at saturation are obtainable from the relation

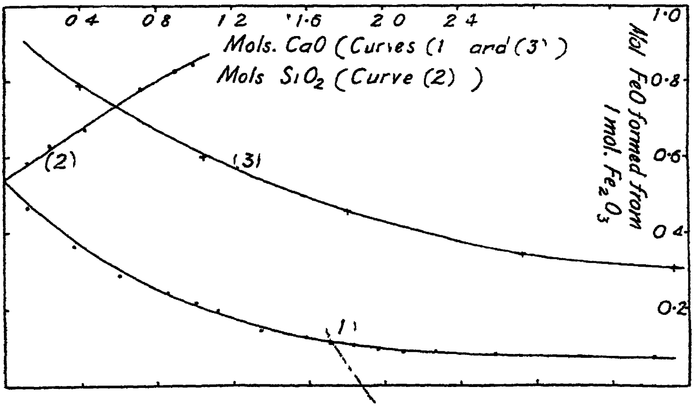

FIG. 2.—Effect of CaO and SiO_2 additions on the dissociations of Fe_2O_3 at 1592° C. in air. Curve (1) CaO addition. Curve (2): SiO_2 addition. Curve (3): CaO addition at constant silica addition of 1·5 mol. Mol. CaO, SiO_2 and FeO are relative to 1 mol. Fe_2O_3 before dissociation.

$$\log x = \frac{L}{4{\cdot}575}\left(\frac{1}{T_m} - \frac{1}{T}\right), \qquad . \quad . \quad . \quad (1)$$

where L is the latent heat of fusion of the pure solute, T_m its melting point and x its activity in the liquid phase at saturation at temperature T, always assuming that no change in the activity of the solid in contact with the solution occurs. This assumption is probably justifiable where no evidence of solid solubility can be detected. The object of the present work has been to derive constants which would lead to a consistent interpretation of all three types of equilibria.

As in the previous paper,[1] the guiding principle has been the observation that qualitatively the effect of additions to iron oxide-containing slags is always in the same sense as would be expected if compounds of the same type as occur in solidified slags were formed. Fig. 2 illustrates the effect of CaO and SiO_2 additions on the reversible dissociation of liquid iron oxide at 1592° C. at the oxygen pressure of the atmosphere. The degree of dissociation decreases with increasing CaO content and increases with increasing SiO_2 content suggesting that equilibrium is displaced in the one case by the formation of calcium ferrites and in the other by the formation of ferrous silicates.

At constant temperature and amount of addition, the degree of dissociation increases with decreasing oxygen pressure as shown in Fig. 1 for the case of iron oxide alone. It was shown in the previous paper that this latter variation could be accounted for by postulating that molecules of FeO, Fe_2O_3 and Fe_3O_4 were all present in the liquid, the equilibrium between them and the oxygen pressure of the atmosphere being defined by the reversible reactions :*

$$Fe_2O_3 = 2FeO + \tfrac{1}{2}O_2 ; \qquad K_F = \frac{(F')^2 \times \sqrt{P}}{(F)}$$

$$Fe_3O_4 = FeO + Fe_2O_3 ; \qquad K_{F'F} = \frac{(F')\,(F)}{(F'F)}$$

where activities are expressed as molar fractions.

The effect of CaO was accounted for by postulating the two additional equilibria :

$$CaO.Fe_2O_3 = CaO + Fe_2O_3 ; \quad K_{CF} = \frac{(C)\,(F)}{(CF)}$$

$$2CaO.Fe_2O_3 = 2CaO - Fe_2O_3 ; \; K_{C_2F} = \frac{(C)^2\,(F)}{(C_2F)},$$

and of SiO_2 by :

$$FeO.SiO_2 = FeO + SiO_2 ; \qquad K_{F'S} = \frac{(F')\,(S)}{(F'S)}$$

$$2FeO.SiO_2 = 2FeO + SiO_2 ; \quad K_{F'_2S} = \frac{(F')^2\,(S)}{(F'_2S)}.$$

When both CaO and SiO_2 were present, all six equilibria had to be considered as existing in the liquid, and in addition,

$$CaO.SiO_2 = CaO + SiO_2 ; \qquad K_{CS} = \frac{(C)\,(S)}{(CS)},$$

$$2CaO.SiO_2 = 2CaO + SiO_2 ; \quad K_{C_2S} = \frac{(C)^2\,(S)}{(C_2S)}.$$

The values of $K_{F'S}$ and $K_{F'_2S}$ thus obtained were applied to the slag-metal data for FeO-MnO-SiO_2 slags of Krings and Schackmann [6] and Körber and Oelsen.[8]. For this purpose it was assumed that, though the "apparent" values of K_{Mn} and L_{FeO}, expressed in terms of total concentrations of FeO and MnO in the slag, vary with silica content, the "true" values, expressed in terms of the calculated contents of the "free" oxides, should be unaltered. On this basis it was found possible to account for the experimental data of these authors, including the constancy of the apparent values of K_{Mn} and L_{FeO} in silica-saturated slags, in terms of a constant value of K_{Mn} for the equilibrium

$$MnO.SiO_2 = MnO + SiO_2 ; \qquad K_{MS} = \frac{(M)\,(S)}{(MS)},$$

the other possible equilibrium

$$2MnO.SiO_2 = 2MnO + SiO_2 ; \quad K_{M_2S} = \frac{(M)^2\,(S)}{(M_2S)},$$

being neglected on the grounds that M_2S appeared to be highly dissociated.

Essentially the same procedure has been followed in the present work with the added criterion that the dissociation constants evaluated must lead to consistent values of the activity of silica at saturation. This has necessitated certain modifications to the values of some of the previously determined constants (the method being essentially one of trial and error), though none of these changes are of a major character. The chief differences are that $FeO.SiO_2$

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* For the sake of brevity the following contractions have been used throughout the paper: $F = Fe_2O_3$; $F' = FeO$; $F'F = Fe_3O_4$; $C = CaO$; $CF = CaO.Fe_2O_3$; $C_2F = 2CaO.Fe_2O_3$; $S = SiO_2$; $F'S = FeO.SiO_2$; $F'_2S = 2FeO.SiO_2$; $CS = CaO.SiO_2$; $C_2S = 2CaO.SiO_2$; $M = MnO$; $MS = MnO.SiO_2$; $M_2S = 2MnO.SiO_2$; P = oxygen pressure.

is now considered more highly dissociated than previously, this being compensated by increasing the stability of $2FeO.SiO_2$, and that the stability of $MnO.SiO_2$ is now considered as intermediate between that of $FeO.SiO_2$ and $CaO.SiO_2$. The latter order of stability is in agreement with fairly widely held belief. The values of the dissociation constants at 1500, 1600 and 1700° c. are shown in Table I.

TABLE I

DISSOCIATION CONSTANTS OF POSTULATED SLAG COMPOUNDS

°c.	F*	$F'F$	CF	C_2F	$F'S$	F'_2S	MS	M_2S	CS	C_2S
1500 ..	—	—	—	—	1·595	0·0777	0·160	0·00200	0·0126	0·0033
1600† ..	0·385	0·239	0·0422	0·142	1·000	0·114	0·100	0·00243	0·017	0·0050
1700 ..	0·992	0·251	—	—	0·661	0·160	0·066	0·00283	0·0223	0·0072
Heat of Dissociation cal./mol. ..	64,000	3,500	—	—	−30,500	25,000	−30,800	10,900	20,000	27,200

* Oxygen pressure measured in cm. Hg.
† 1592° c. of iron-oxide dissociation experiments taken as nominal 1600° c.

A point of some significance is that the best values of the constants at the different temperatures have generally been found to give a reasonably straight line plotted logarithmically against $1/T°$ K. this enabling heats of dissociation to be evaluated. Somewhat surprisingly some of these are negative. From the point of view of saturation this has been found likely to occur whenever the compound involved melts incongruently owing to the resultant trend of the liquidus curve. That it is not conditioned by the saturation requirement, however, is shown by the fact that similar tendencies were shown (e.g., by K_{FS}) in the previous work, which was based solely on a consideration of iron-oxide dissociation data.

Calculated curves corresponding to the above constants are shown compared with experimental data in Fig. 1, 2, 3 and 4.

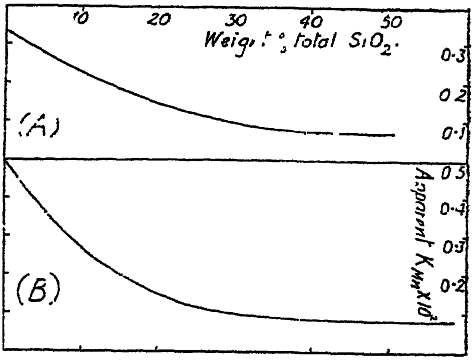

FIG. 3.—Effect of silica addition on "apparent" value of K_{Mn}. (A) Experimental curve of Krings and Schackmann[6] at 1550° c. (B) Calculated curve at 1600° c.

The agreement between theoretical and experimental values is in all cases reasonably good, indicating that one set of constants is capable of accounting for the three kinds of heterogeneous equilibria of the slag considered. In Fig. 1, the dissociation curve of iron oxide at 1592° c. has been constructed, using K_F and K_{FF}, down to the composition at which oxygen-saturated metallic iron separates, this point being calculated assuming the oxygen pressure of the latter phase at 1600° c to be $0{\cdot}8 \times 10^{-8}$ atm. as indicated by Chipman's data.[15] The calculated oxygen-content of the oxide at this point corresponds to a ferric oxide content of 2·2 % as compared to the value of 6·0 %, given by Fetters and Chipman.[16]

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[16] Fetters and Chipman, *Trans. Amer. Inst. Min. Met. Eng.*, 1941, **145**, 95.

Fig. 2 shows the calculated effects of CaO and SiO_2 additions on the dissociation of iron oxide as compared with points derived from the experimental data Fig. 3 (B) shows the calculated variation of "apparent" K_{Mn} with silica content at 1600° c. for FeO-MnO-SiO_2 slags over a bath containing 0·1 % Mn. Körber and Oelsen's value [3] of 0·00494 in simple FeO-MnO slags was assumed to be correct (concentrations as molar fractions in the slag) and it was assumed that "true" K_{Mn} in acid slags would have the same value when expressed in terms of the calculated contents of "free" FeO and MnO. The value of "apparent" K_{Mn} at saturation with silica is approximately 0·0008 at this content of Mn as compared to 0·00082 as determined experimentally by Körber and Oelsen.[8] Kring's and Schackmann's curve [6] of K_{Mn} against silica content at 1550° c. is shown in Fig. 3 (A).

Slag constitutions and values of apparent K_{Mn} and L_{FeO} calculated for the case of silica-saturated FeO-MnO-SiO_2 slags are shown in Table II. Apparent K_{Mn} and L_{FeO} were calculated on the basis of weight fractions in both slag and metal. Körber and Oelsen's experimental values in silica-saturated slags [8] were :

TABLE II

Temp.	[Mn] Wt. %	True K_{Mn}*	True L_{FeO}*	Slag Constitution (Molar Fractions)							FeO Wt. %	MnO Wt %	Apparent K_{Mn}	Apparent L_{FeO}
				S	F'	$F'S$	F'_2S	M	$M'S$	M'_2S				
1500 c. . .	0·1	0·0035	0·0020	0·448	0·1088	0·0306	0·0687	0·0315	0·0883	0·2230	17·8	36·1	0·00050	0·0012
1600 c. . .	0·1	0·0049	0·0033	0·509	0·1152	0·0586	0·0596	0·0233	0·1188	0·1154	21·3	26·6	0·0008	0·0018
1600 c. . .	0·2	0·0049	0·0033	0·509	0·0721	0·0367	0·0254	0·0292	0·1486	0·1800	11·1	37·0	0·0006	0·0021
1700 c. . .	0·1	0·0072	0·0048†	0·589	0·1016	0·0903	0·0380	0·0141	0·1260	0·0414	21·9	18·0	0·0012	0·0023

* Values of Körber and Oelsen [8] and Korber [4] for simple FeO-MnO slags. Activities as molar fractions in slag.

† Value raised from 0·0045 to fit required exponential relation with 1/T° K

	1500° c.	1600° c.	1700° c.
Apparent K_{Mn}	0·0005 . .	0·000825 . .	0·00139
Apparent L_{FeO}	0·0013 . .	0·0021 . .	0·0030

These values were claimed to be independent of the MnO/FeO ratio (or [Mn]). The calculated values, however, show a slight drift with MnO/FeO ratio as shown by the values at 1600° c. Further examples of calculated constitutions are given in the Appendix.

Fig. 4 (A) shows calculated and experimental curves of silica-saturation for the systems CaO-SiO_2,[17, 18] MnO-SiO_2[19] and FeO-SiO_2[18, 20]. The molar fractions of "free" silica corresponding to the calculated saturation points at 1500°, 1600° and 1700° c. are as follows:

	1500° c.	1600° c.	1700° c.
(S) . .	0·448 . .	0·509 . .	0·589

these values being obtained in the process of "fitting" the experimental liquidus curves. Only in the case of the MnO-SiO_2 curve is there an appreciable difference from the experimental curve. As, however, the latter was determined by the method of heating and cooling curves it is probably somewhat qualitative. The calculated curve of silica-saturation at 1600° c. in FeO-MnO-SiO_2 slags is shown in Fig. 4 (B) compared with Körber and Oelsen's suggested mean saturation curve over the range 1550°–1650° c.[8]

Activity of Silica in CaO–SiO₂ Slags

Fig. 5 shows the calculated variation with composition of the molar fractions (activities) of the various molecular species postulated in liquid CaO-SiO_2 slags at 1600° c. as calculated from the values of K_{CS} and K_{C_2S} given in Table I.

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[17] Rankin and Wright, *Amer. J. Sci.*, 1915, **39**, 1.

[18] Greig, *Amer. J. Sci.*, 1927, **13**, 1.

[19] White, Howat and Hay, *J. Roy. Tech. College, Glasgow*, 1934, **3**, 231.

[20] Bowen and Schairer, *Amer. J. Sci.*, 1932, **24**, 177.

Compositions beyond the saturation limits indicated are, of course, unrealisable in practice. Saturation with C_2S is reached at $(C_2S) = 0{\cdot}283$, $(C) = 0{\cdot}166$ and $(S) = 0{\cdot}051$. In any slag, therefore, saturation with C_2S should occur when the "solubility product"

$$(C)^2 \times (S) = 0{\cdot}005 \times 0{\cdot}283 = 0{\cdot}00142$$

Saturation with silica, as stated above, occurs at $(S) = 0{\cdot}509$. Lo Ching Chang and Derge [11] determined the activity of silica in CaO-SiO$_2$ slags of various compositions at 1600° c. If their values, which are relative to β-cristobalite as unity, are multiplied by 0·509 direct comparison with the silica activity curve of Fig. 6 can be made The values so obtained, as shown, follow the present curve closely apart from a deviation at the composition of CaO.SiO$_2$. This can be explained, as suggested by these authors, if some association of CaO.SiO$_2$ molecules occurs. Apart from this discrepancy it would appear that the present model gives a true indication of the activity of silica in these slags.

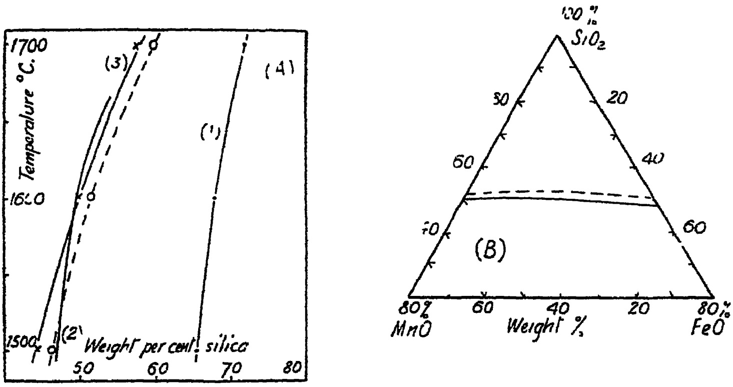

FIG. 4.—(A) Liquidus curves of systems (1) CaO—SiO$_2$, (2) MnO—SiO$_2$, (3) FeO—SiO$_2$. Calculated points: ● CaO—SiO$_2$, ⊙ MnO—SiO$_2$, × FeO—SiO$_2$.
(B) Calculated curve of silica-saturation in system FeO—MnO—SiO$_2$ (broken line). Solid line shows limiting concentration reached in Körber and Oelsen's slags at 1550°–1650° c.[8]

Partial molal free energies of silica calculated from the present data are also in reasonable agreement with Chang and Derge's as indicated by the following figures:

Total Silica Content (Mol).		0·533		0·583	
Temp. ° c.		1600° c.	1700° c.	1600° c.	1700° c
Partial Molal	Present data	2580 ..	3130 ..	1135 ..	1950
Free Energy (cal.)	Chang and Derge	2400 ..	3600 ..	1290 ..	2130

Partial molal heat contents are also in reasonable agreement at silica contents approaching saturation, e.g., the present data gives 13,350 cal. at 0·60 mol. total silica as compared with 14,700 cal. at 0·583 mol. SiO$_2$ from Chang and Derge's data. The latter, however, found that heat contents increased with decreasing silica content, whereas the present values tend to decrease. This may indicate that the values attributed to K_{C_2S} are not yet completely satisfactory.

As stated above, the values obtained for the activity of silica at saturation are 0·448, 0·509 and 0·589 at 1500°, 1600° and 1700° c. These values (see eqn. (1)) would indicate that silica melts at 2250° c. with a latent heat of 9400 cal./mol. and an entropy change of 3·72 cal./° c. The actual melting point of silica is 1728° c. on the International Temperature Scale and the latent heat of fusion is approximately 6800 cal./mol.[21] giving an entropy change of 3·4 cal./° c. The explanation of these apparent anomalies would appear to be in the non-ideal behaviour of silica associated with the occurrence of immiscibility in the liquid state. According to this view the relatively low melting point of silica is due to the fact that it melts to give a highly polymerised liquid phase. The initial depression of the freezing point by small additions of CaO, FeO, etc. is associated with melting to this highly polymerised form and corresponds to a latent heat of 6800 cal. At higher contents of these additions, depolymerisation occurs with an abrupt discontinuity in the liquidus curve and separation into two liquid phases. Al_2O_3, on the other hand, gives a rather more rapid depression of the freezing point than corresponds to a latent heat of 6800 cal., this behaviour being consistent with its known capacity for taking part in the formation of silicate networks.

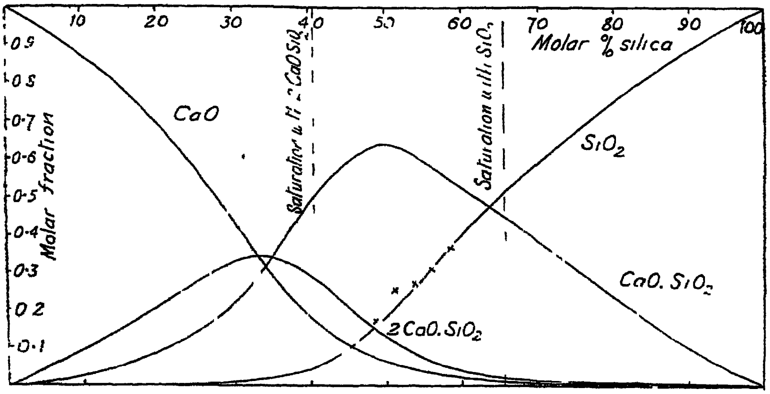

FIG. 5.—Calculated activities (molar fractions) of molecular species in $CaO-SiO_2$ melts at 1600° c. × Silica activities from Lo Ching Chang and Derge.[13]

Application to Basic Slags

As shown in Fig. 1, calculations using the determined values of K_F and $K_{F'F}$ indicate that there should be 2·2 % Fe_2O_3 in the oxide in equilibrium with metallic iron at 1600° c. At this point the reaction

$$3FeO = Fe + Fe_2O_3 ; \quad K_{F'} = \frac{(F)}{(F')^3}$$

occurs, the value of which according to the present calculations should be 0·002 approximately.

Utilising the finding of Fontana and Chipman [22] that the solution of oxygen in liquid iron is an ideal one the effect of CaO on the total Fe_2O_3 content of the oxide in equilibrium with metallic iron can be calculated. The results of this calculation are shown in Fig. 6 in which the ferric oxide content is plotted as the ratio to that present in a pure iron oxide slag. The curve obtained is in good agreement with the data of Fetters and Chipman [16] plotted similarly, showing that the present constants give agreement with experiment as regards the relative effects of CaO. The *actual* Fe_2O_3 contents are, however, considerably lower than were found by these workers this being due to the low Fe_2O_3 content predicted in pure iron oxide. It would appear, therefore, that some revision of K_F, $K_{F'F}$ and $K_{F'}$ is necessary. The probable reason for this is the error caused by the pick-up of iron by the platinum crucibles at low oxygen pressures in the iron-oxide dissociation experiments, for which no allowance was made in deriving the constants. It is intended, therefore, to carry out a revision of these constants.

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[21] Ray, *Proc. Roy. Soc. A*, 1922, **101**, 509.

[22] Fontana and Chipman, *Trans. Amer. Soc. Met.*, 1936, **24**, 313.

Preliminary calculations on the phosphorus reaction have, however, been carried out using the present constants. The results indicate that it should be possible to evaluate a "true" constant for this reaction in terms of the present model, and this work will be extended when revision of the constants has been made.

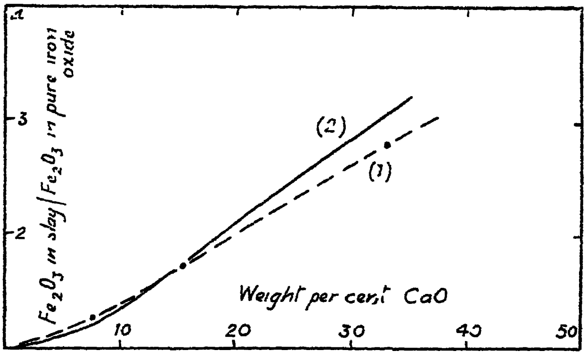

FIG. 6.—Effect of CaO addition on total Fe_2O_3 content of iron oxide in equilibrium with metallic iron. (1) Calculated curve. (2) Curve from Fetters and Chipman.[15]

Conclusions

Using what they regard as a purely formal model for the constitution of liquid slags the authors have sought to show that equilibrium slag-metal, slag-atmosphere and slag-refractory relationships can be accounted for in terms of calculated activities of the slag reactants. Though some revision of the constants seems necessary it has been shown that a considerable measure of success in predicting experimental relationships can be achieved. It is not considered that the model represents a true picture of the constitution of liquid slags and it is believed that ultimately an electrochemical approach will prove more acceptable.

The authors take pleasure in acknowledging that one of them (P.M.) was in receipt of a Research Bursary of the Steel Castings Division of the British Iron and Steel Research Association while this work was being carried out.

They should also like to acknowledge the assistance of Miss Sylvia Judge in the preparation of the manuscript.

Appendix

EXAMPLES OF CALCULATED CONSTITUTIONS OF LIQUID SLAGS

(1) *Dissociation of liquid iron oxide at* 1592° C. (Fig. 1.)

Oxygen Pressure (atm.)	Molar Fractions in Slag			Wt. % O_2 in Oxide
0·341	0·457F;	0·357$F'F$;	0·186F'	28·25
1·033	0·521F;	0·329$F'F$;	0·150F'	28·30

(2) *Dissociation of iron oxide at* 1592° C. *in air in presence of CaO* (Fig. 2, Curve (1))

Mol. Fractions in Slag: 0·100F, 0·415$F'F$, 0·0982F', 0·386CF, 0·211C_2F, 0·163C.

Total Mol. CaO = 1·200 } Both relative to 1 mol.
Total Mol. FeO = 0·174 } Fe_2O_3 initially.

(3) *Dissociation of iron oxide at* 1592° C. *in air in presence of* SiO_2
(Fig. 2, Curve (2))

Molar Fractions in Slag : 0·228F, 0·143$F'F$, 0·150F', 0·532$F'S$, 0·070F'_2S, 0·355S.

$$\left.\begin{array}{lcl}\text{Total Mol. } SiO_2 & = & 0{\cdot}776 \\ \text{Total Mol. } FeO & = & 0{\cdot}794\end{array}\right\} \begin{array}{l}\text{Both relative to 1 mol.} \\ \quad Fe_2O_3 \text{ initially.}\end{array}$$

(4) *Dissociation of iron oxide at* 1592° C. *in air in presence of CaO and* SiO_2
(Fig. 2, Curve (3))

Molar Fractions in Slag: 0·101F, 0·0424$F'F$, 0·100F', 0·121CF, 0·020C_2F, 0·050C, 0·3585CS, 0·061C_2S, 0·012$F'S$, 0·0107F'_2S, 0·122S.

$$\left.\begin{array}{lcl}\text{Total Mol. } CaO & = & 1{\cdot}855 \\ \text{Total Mol. } SiO_2 & = & 1{\cdot}485 \\ \text{Total Mol. } FeO & = & 0{\cdot}472\end{array}\right\} \begin{array}{l}\text{All relative to 1 mol.} \\ \quad Fe_2O_3 \text{ initially.}\end{array}$$

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THE BEHAVIOUR OF OXYGEN IN LIQUID STEEL DURING THE REFINING PERIOD IN THE BASIC OPEN-HEARTH FURNACE *

BY S. FORNANDER

Received 29th July, 1948

In the following an account is given of a part of the results obtained during the investigation. Attention will be focused on the influence of the manganese content of the charge upon the oxygen content of the steel bath as well as upon the carbon reaction :

$$\text{C (in liquid Fe)} + \text{O (in liquid Fe)} = \text{CO } (g).$$

During the later years before the war a few papers were published in Germany on the role of manganese in the basic open-hearth process. Bardenheuer and Thanheiser,[1] who studied the refining process with special reference to the oxygen content of the steel bath came to the following conclusions. At carbon contents higher than 0·2 % the oxygen content of the steel bath is determined by the carbon content only : carbon and oxygen were supposed to react very rapidly with each other. At lower carbon contents the oxygen content of the steel was said to be determined by the FeO content of the slag. Further, they assumed that at lower carbon contents the oxygen content was influenced by manganese in such a way that it was decreased if the manganese content was increased. The reason for this was assumed to be that a high MnO content in the slag has a diluting

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[1] Bardenheuer and Thanheiser, *Mitt. Kaiser-Wilhelm Inst. Eisenforsch.*, 1935, 17, 133.

* The investigation described in this paper was carried out by a Committee reporting to *Jernkontorets Forskningsverksamhet* (The Research Organisation of the Swedish Ironmasters' Association). The Committee's terms of reference were " to study the role of manganese in the basic open-hearth process and the possibility of economising in manganese." The following have been members of the Committee : I. Bohm, G. Helmer, S. von Hofsten, B. Kalling, G. Phragmén, T. Collén, N. Rudberg and the author. The work on that part of the investigation which is described here was started in 1942. The most important results obtained concern the question of the oxygen content of the steel bath during the refining period.

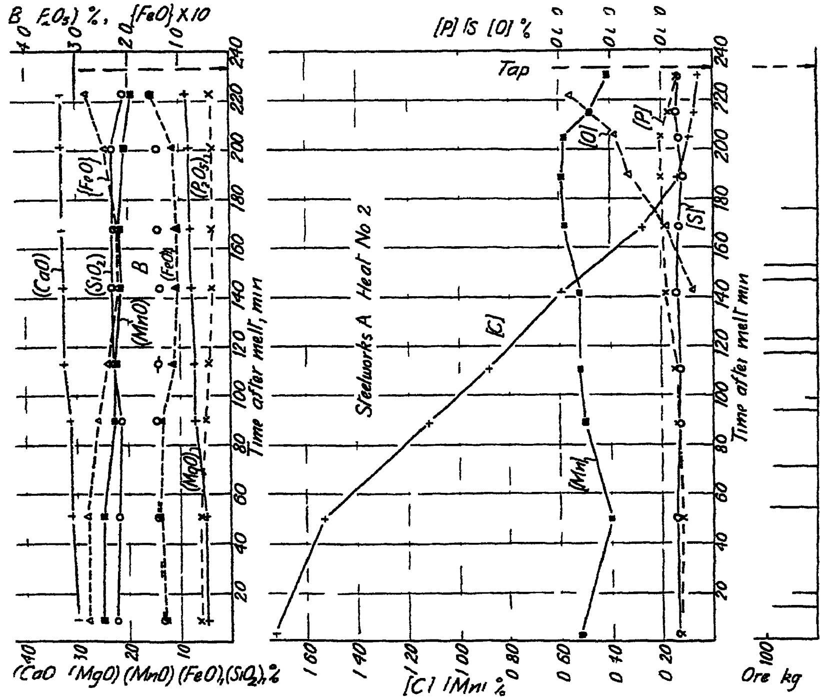
B (P2O5) %, {FeO} X 10
(CaO) (MgO) (MnO) (FeO) (SiO2) %
(CaO)
(SiO2)
(FeO)
(MnO)
B
(Fe2O3)
(P2O5)
(MgO)
Time after melt, min
Steelworks A Heat No 2
[P] [S] [O] %
Tap
[C]
[Mn]
[O]
[P]
[S]
[C] [Mn] %
Time after melt min
Ore kg

FIG 2

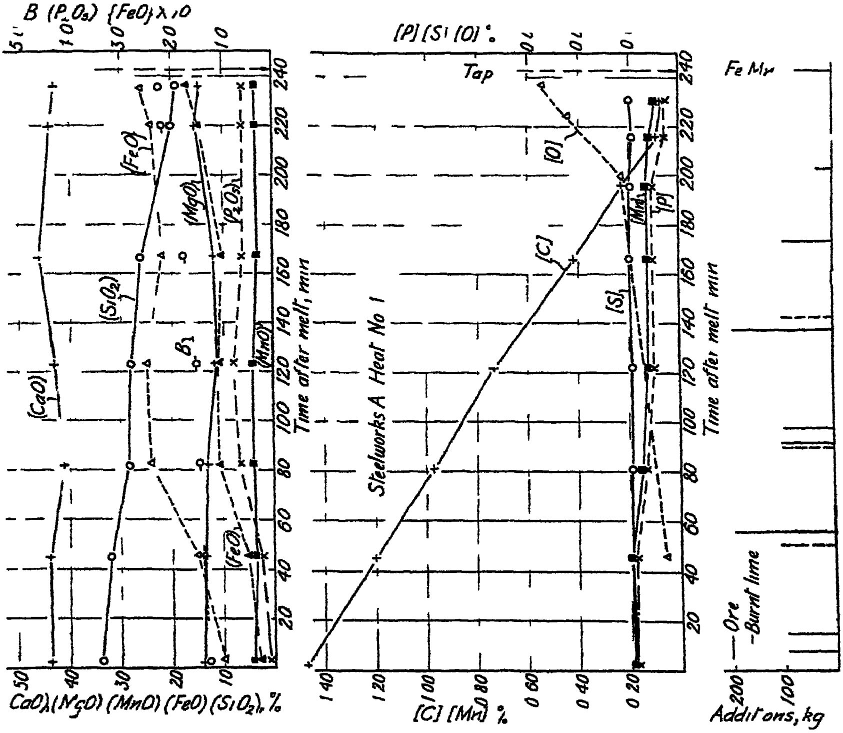
B (P2O5) {FeO} X 10
(CaO) (MgO) (MnO) (FeO) (SiO2) %
(CaO)
(SiO2)
(FeO)
(MgO)
(P2O5)
B
(Fe2O3)
(MnO)
Time after melt, min
Steelworks A Heat No 1
[P] [S] [O] %
Tap
[O]
[C]
[S]
[Mn]
[P]
[C] [Mn] %
Time after melt min
Fe Mn
Ore
Burnt lime
Additions, kg

FIG I

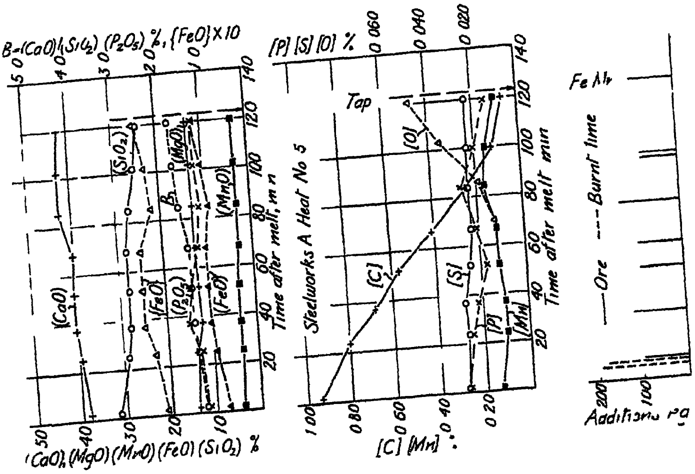

FIG. 5

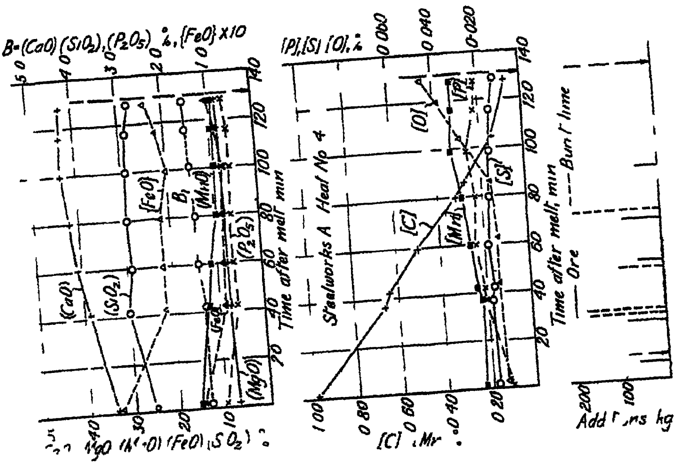

FIG. 4

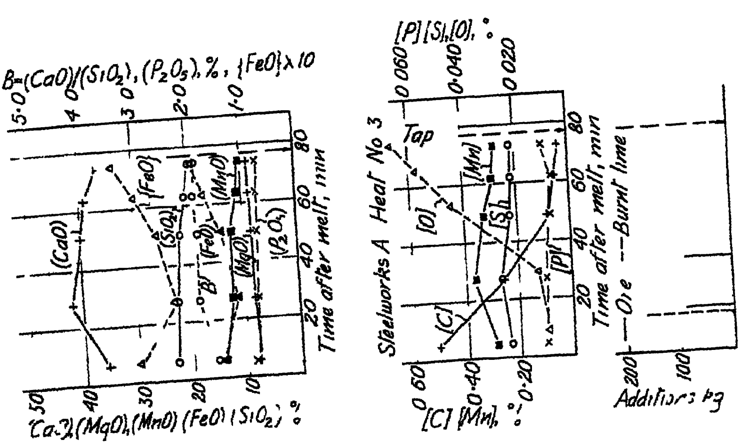

FIG. 3.

effect upon the FeO content, and that as a consequence the capacity of the slag to transfer oxygen to the steel bath was reduced. Further it was stated that this circumstance would affect the rate of carbon-drop in such a way that the higher the manganese content of the charge the lower the rate of carbon-drop. Finally, reduction of manganese from the slag was said to be a distinctive feature of a low oxygen content in the bath.

These conclusions have wholly, or partly, served as a hypothesis of work in German investigations published later[2] [3] [4] [5] and they may therefore be regarded as accepted during later years, at least as far as Germany is concerned.

However, the conclusions mentioned cannot be accepted without reservation, foremost because the method of sampling used by Bardenheuer and Thanheiser does not seem to be free from objections with regard to analysis for oxygen. The steel sample was taken from the furnace with the usual test spoon, was "killed" with aluminium and poured into a copper mould with thick walls. Table I shows a few examples of analyses obtained with this method. The equilibrium value of the product [C] × [O] in liquid steel is not lower than about 0·0020. Therefore, if a lower value of this product is obtained in a steel sample, taken out from a "boiling" steel bath, this implies that either the method of sampling or the method of analysis has been unsuitable. In the examples shown in Table I, it is probably the sampling method that has given too low values of the oxygen content—and also of the carbon content—in consequence of the fact that carbon monoxide has been evolved from the steel in the test spoon before the aluminium addition has been made.

TABLE I

ANALYSES OF SAMPLES, REPORTED BY BARDENHEUER AND THANHEISER[1]

Heat No	Sample No	[C]	[O]	[C] × [O]
I	7	0·07	0·010	0·0007
II	1	0·19	0·006	0·0011
IV	4	0·22	0·007	0·0015
IV	6	0·11	0·014	0·0015
VI	26	0·44	0·003	0·0013

Experimental and Results

The results obtained in this investigation are based on 36 experimental heats made at four Swedish steelworks. The heats had different manganese contents in the charge ranging between 0·15 and 2·30 %, and the intention was that the results should show what influence a high or low manganese content in the charge has upon the refining process in the furnace. For ten of the experimental heats, diagrams are given showing the variation of the concentrations in steel and slag during the course of the heats, see Fig. 1–10.

The steel samples were taken with a sampling device, suggested by Rudberg and shown in Fig. 11. The mould was made from mild steel. Inside the mould was placed an aluminium wire of 1 mm. diam., folded in such a way that it could easily be dissolved in the steel. The mould was covered by a lid of sheet steel of 0·5 mm. thickness. On top of the lid was placed a cylinder, kept in position by an iron wire. According to the original suggestion the cylinder was to have been made from fire-clay or graphite. For taking samples in the open-hearth furnace it has been found, however, that it is better to make the cylinder from wood, for otherwise the iron wire becomes so well slagged, when the mould passes the slag layer that it does not melt. A sample is taken in the following way. When the mould has been slagged rapidly and carefully up to the edge, it is dipped into the steel bath. After 1–2 sec. the iron wire melts off and the wooden cylinder rises to the surface. The sheet lid, which is now uncovered, melts and the mould becomes filled with steel. If the sampling is done in this way, samples free from furnace slag will be obtained.

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[2] Bardenheuer and Thanheiser, *Mitt. Kaiser-Wilhelm Inst. Eisenforsch.*, 1938, **20**, 67.

[3] Bardenheuer and Henke, *Mitt. Kaiser-Wilhelm Inst. Eisenforsch.*, 1939, **21**, 243.

[4] Wilhelm, *Stahl Eisen*, 1936, **56**, 1423.

[5] Kreutzer, *Stahl Eisen*, 1939, **59**, 1017.

In some of the experimental heats, on 39 occasions duplicate samples were taken, one immediately after the other with the sampling mould. The small sample ingots obtained were analysed for oxygen with the vacuum-fusion method. In 38 of the cases the agreement between the two samples was satisfactory, the greatest difference between the oxygen values obtained being 0·003 % O. This is regarded as proof that the sampling method gives reproducible results. The slag samples were taken with a test spoon in the usual way and poured out into a flat mould of about 5 in. diam

At the time when the majority of the experimental heats were carried out we had no reliable method for temperature measurement of liquid steel in Sweden. Therefore it was not until recently that temperature measurements were made on four of the heats. The determinations were carried out with quick-immersion pyrometers of a design slightly modified from that developed in Britain by Schofield and Grace. The design of the pyrometers is described elsewhere.[6]

The Carbon Reaction. Oxygen in the Steel Bath

Influence of Manganese. The most important of the reactions occurring in the basic open-hearth furnace during the refining period is the carbon reaction :

C (in liquid Fe) + O (in liquid Fe) = CO (*g*). The equilibrium constant *K* for the carbon reaction can be expressed as :

$$K = \frac{|\mathrm{CO}|}{\{\mathrm{C}\}\ \{\mathrm{O}\}}, \text{or } K\{\mathrm{C}\}\{\mathrm{O}\} = |\mathrm{CO}|,$$

where $\{\mathrm{C}\}$ = the activity of carbon in the liquid steel,
$\{\mathrm{O}\}$ = the activity of oxygen in the liquid steel,
$|\mathrm{CO}|$ = partial pressure of CO in the gas phase, i.e., the gas bubbles in the liquid steel.

The equilibrium of the reaction has been studied by several investigators. The first successful determinations were made by Vacher and Hamilton,[7] by Vacher,[8] and by Phragmén and Kalling.[9] The results of their experiments can be summed up in the following way. The product of the carbon and oxygen contents in liquid steel is constant at equilibrium and therefore independent of the carbon content. Consequently, at higher carbon contents the oxygen content is low, and at lower carbon contents the oxygen content is high.

The latest investigation done in this field was made by Marshall and Chipman.[10] They used a furnace permitting experiments at various pressures of the gas phase up to 20 atm. According to their results the value of the carbon-oxygen product is not the same at different carbon contents but increases with the carbon content. From their data the value of the product at different carbon contents can be computed. One finds at 1600° c.

[C]	[C] × [O]
0·02	0·0019
1·00	0·0036

That the carbon-oxygen product increases with the carbon content can be explained by assuming that the steel is capable of dissolving a certain amount of CO as such. The value obtained by Marshall and Chipman for the CO solubility in liquid steel is 0·0028 %.

In Fig. 12 the oxygen content of the steel in the experimental heats is plotted against the carbon content, and in Fig. 13 the product [C] × [O] is plotted against the carbon content. Fig. 12 shows the well-known fact that the oxygen content

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[6] Fornander, *Jernkont. Ann.*, 1947, **131**, 225.
[7] Vacher and Hamilton, *Trans. Amer. Inst. Min. Met. Eng.*, 1931, **95**, 124.
[8] Vacher, *U.S. Bur. Stand. J. Res.*, 1933, **11**, 541.
[9] Phragmén and Kalling, *Jernkont. Ann.*, 1939, **123**, 199.
[10] Marshall and Chipman, *Trans. Amer. Soc. Met.*, 1942, **30**, 695.

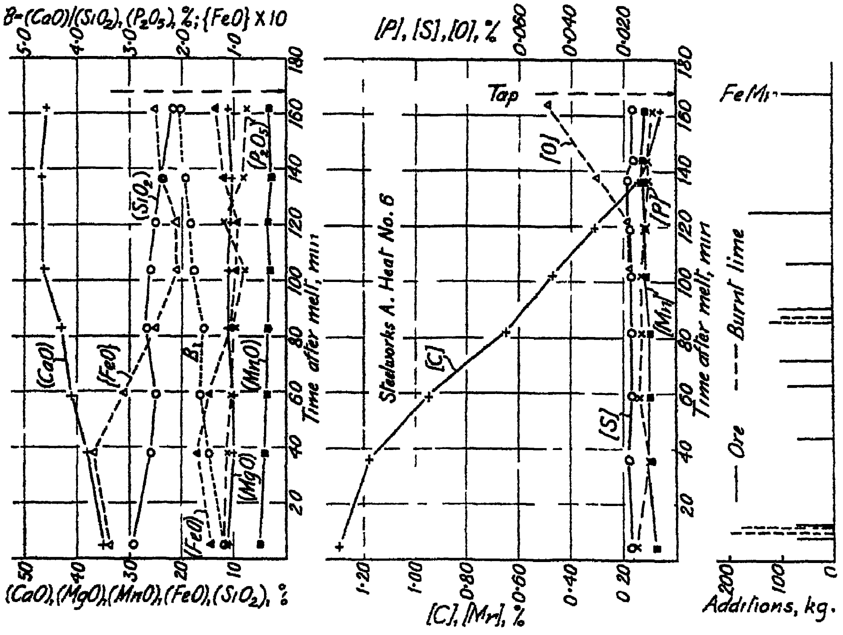
B=(CaO)/(SiO₂), (P₂O₅), %; {FeO} X 10
5·0
4·0
3·0
2·0
1·0
(CaO), (MgO), (MnO), (FeO), (SiO₂), %
50
40
30
20
10
(CaO)
{FeO}
(SiO₂)
B
(P₂O₅)
(MnO)
(MgO)
(FeO)
Time after melt, min
20
40
60
80
100
120
140
160
180
Steelworks A. Heat No. 6
[P], [S], [O], %
0·060
0·040
0·020
[C], [Mn], %
1·20
1·00
0·80
0·60
0·40
0·20
Tap
[O]
[C]
[S]
[Mn]
[P]
FeMn
Burnt lime
Ore
200
100
0
Additions, kg.

FIG. 6.

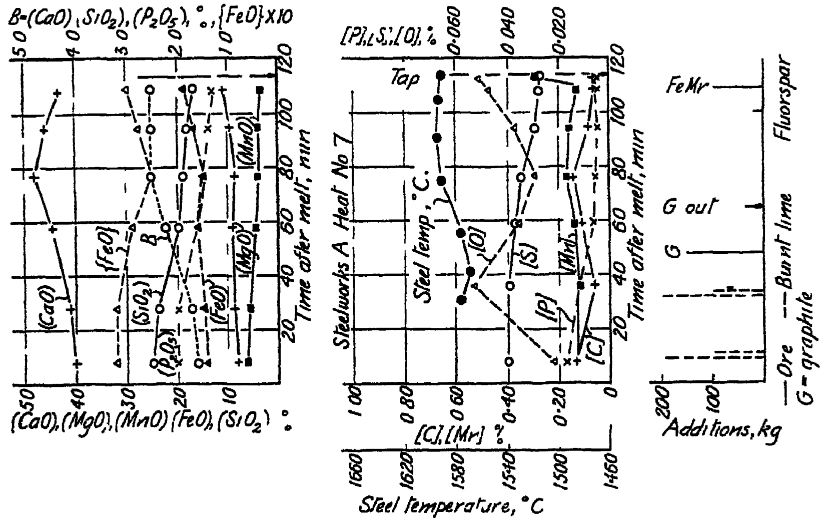
B=(CaO)/(SiO₂), (P₂O₅), %, {FeO} X 10
5 0
4 0
3 0
2 0
1 0
(CaO), (MgO), (MnO) (FeO), (SiO₂) %
50
40
30
20
10
(CaO)
{FeO}
(SiO₂)
B
(P₂O₅)
(FeO)
(MgO)
(MnO)
Time after melt, min
20
40
60
80
100
120
Steelworks A Heat No 7
[P], [S], [O], %
0·060
0·040
0·020
[C], [Mn] %
1·00
0·80
0·60
0·40
0·20
0
Steel temperature, °C
1660
1620
1580
1540
1500
1460
Tap
Steel temp, °C.
[O]
[S]
[Mn]
[P]
[C]
FeMn
G out
G
Fluorspar
Burnt lime
Ore
G = graphite
200
100
Additions, kg

FIG. 7.

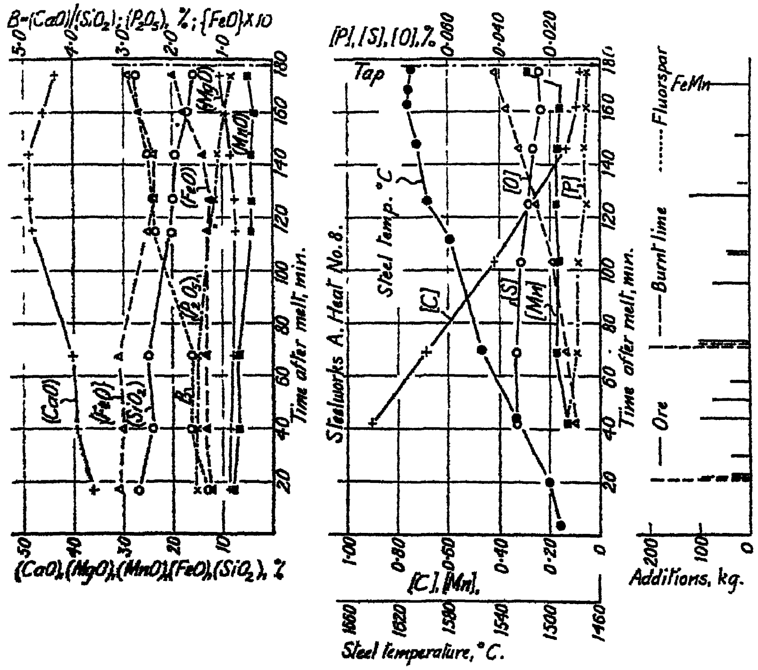
B-(CaO)/(SiO$_2$):(P$_2$O$_5$). %; {FeO}x10
(CaO),(MgO),(MnO),(FeO),(SiO$_2$), %
(CaO)
(FeO)
(SiO$_2$)
B
(P$_2$O$_5$)
(MgO)
(MnO)
Time after melt, min.
Steelworks A. Heat No.8.
[P],[S],[O],%
Tap
Steel Temp. °C
[C]
[S]
[Mn]
[O]
[P]
[C],[Mn],%
Steel temperature, °C.
Ore
Burnt lime
Fluorspar
FeMn
Additions, kg.

FIG. 8.

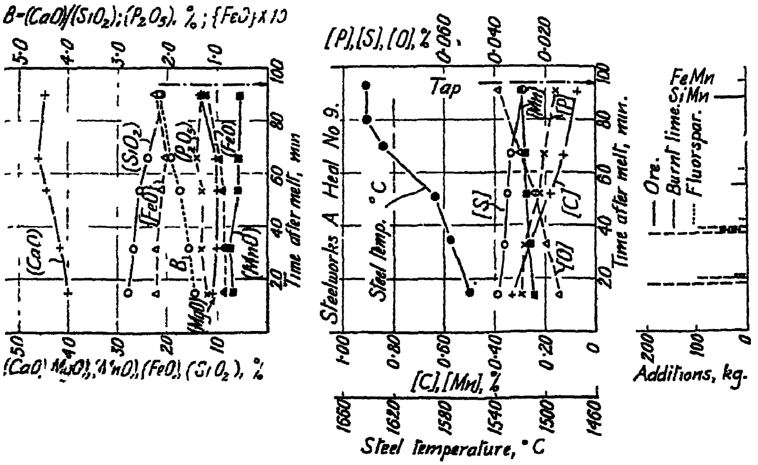
B-(CaO)/(SiO$_2$):(P$_2$O$_5$). %; {FeO}x10
(CaO),(MgO),(MnO),(FeO),(SiO$_2$), %
(CaO)
(SiO$_2$)
(FeO)
B
(P$_2$O$_5$)
(MgO)
(MnO)
(FeO)
Time after melt, min
Steelworks A Heat No 9.
[P],[S],[O],%
Tap
Steel Temp. °C
[S]
[Mn]
[P]
[C]
[O]
Time after melt, min.
[C],[Mn],%
Steel Temperature, °C
Ore.
Burnt lime.
Fluorspar.
FeMn
SiMn
Additions, kg.

FIG. 9.

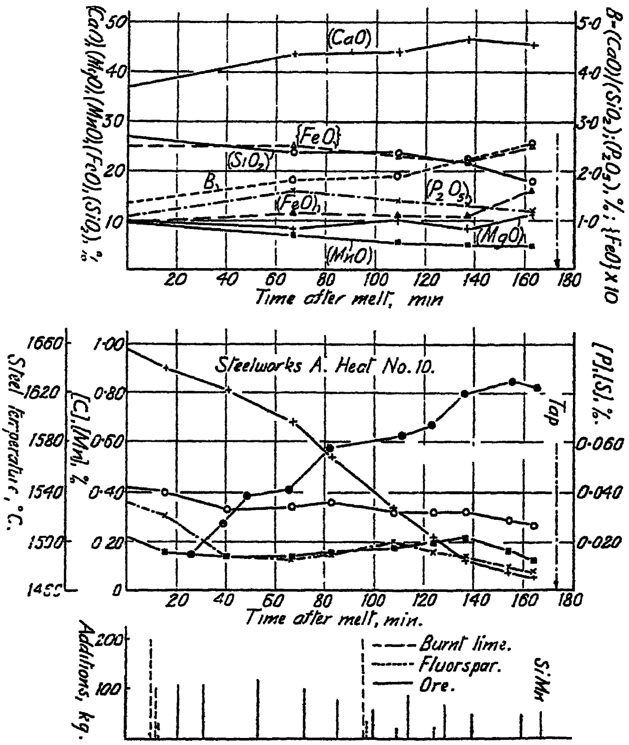

Fig. 10.

during the refining period is higher than the equilibrium value. At carbon contents lower than *ca.* 0·2 % the "excess oxygen," i.e., the difference between the actual and the equilibrium values, seems to vary slightly between, say, 0·012 and 0·025 % O. This is in general agreement with the results obtained by Brower and Larsen [11] [12] [13] [14]; however, the absolute values of the excess oxygen are lower in this investigation than in those which they have reported, which is probably due to differences in sampling technique. Their sampling technique gave about the same reproducibility as the one used in this investigation; further experiments must be done before a statement can be made as to the absolute accuracy of the two methods.

Fig. 13 seems to show that the values of the product [C] × [O], which are rather scattered at higher carbon contents, approach the equilibrium value at lower carbon contents.

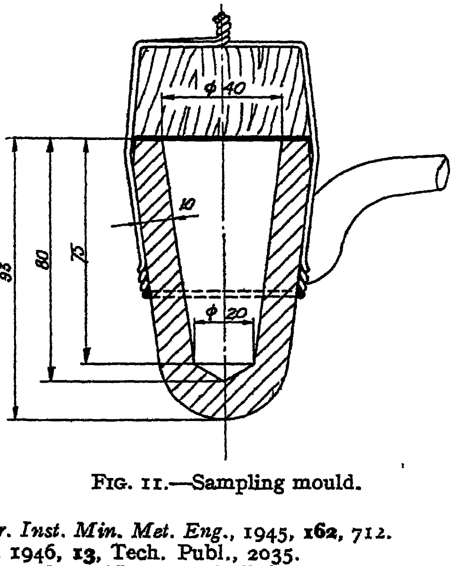

Fig. 11.—Sampling mould.

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[11] Brower and Larsen, *Trans. Amer. Inst. Min. Met. Eng.*, 1945, **162**, 712.
[12] Brower and Larsen, *Met. Tech.*, 1946, **13**, Tech. Publ., 2035.
[13] Brower and Larsen, *Met. Tech.*, 1946, **13**, No. 7, Tech. Publ., 2076.
[14] Larsen, *Trans. Amer. Inst. Min. Met. Eng.*, 1941, **145**, 67.

Fig. 12 and 13 include all the values obtained during the experimental heats, and these had, as mentioned earlier, different manganese contents in the charge, varying between 0·15 and 2·3 % Mn. The diagrams show that the manganese content has no influence upon the oxygen content of the steel during the refining period. Thus, the statement of Bardenheuer and Thanheiser that a high manganese content in the charge would have a depressing effect on the oxygen content in the steel is not supported by the results of this investigation. From the knowledge we have about the deoxidizing power of manganese in comparison with that of carbon, we have also no reason to suspect such an effect: if we take as an example a steel bath at 1600° c. with an oxygen content of 0·040 % O, the equilibrium content of manganese is *ca.* 3 % and that of carbon only *ca.* 0·05 %.[1]

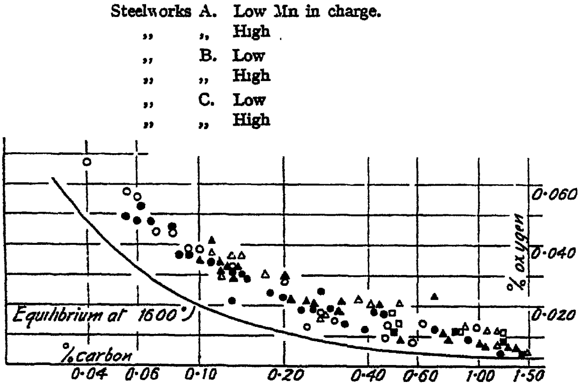

FIG. 12.—Oxygen contents during refining.

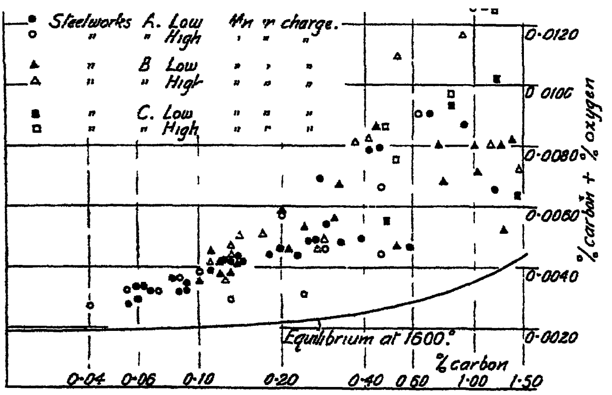

FIG. 13.—[C] × [O] – product during refining.

The factor which has the largest influence upon the oxygen content of the steel, is the carbon content, and this is the case also at carbon contents lower than 0·2 %. Reference is here made to the papers by Körber and Oelsen,[16] by Brower and Larsen,[11 12 13 14], and by Kalling,[17 18 19] who in a logical and illuminating way have discussed the nature and significance of the carbon reaction.

[15] Körber and Oelsen, *Mitt. Kaiser-Wilhelm Inst. Eisenforsch.*, 1932, **14**, 181.

[16] Körber and Oelsen, *Mitt. Kaiser-Wilhelm Inst. Eisenforsch.*, 1935, **17**, 39.

[17] Kalling, *Jernkont. Ann.*, 1934, **118**, 69.

[18] Kalling, *Jernkont. Ann.*, 1936, **120**, 1.

[19] Kalling and Rudberg, *Jernkont. Ann.*, 1937, **121**, 93.

Bardenheuer and Thanheiser stated also that a manganese reduction from the slag was a distinctive feature of a low oxygen content in the bath. From a detailed study of Fig. 13 along these lines one will find that the samples taken during manganese reduction show about the same values of the [C] × [O] product as the rest, and that points from the first-mentioned samples are fairly evenly distributed within the area of scatter.

In Fig. 14 the rate of carbon-drop for the carbon range 0·50 — 0·15 % C has been plotted against the manganese content of the charge. The diagram shows that the manganese content of the charge has no marked effect on the rate of carbon-drop, at least not at manganese contents higher than 0·4 %. Other factors than the manganese content seem to be of first importance for the rate of carbon-drop. The conclusion of Bardenheuer and Thanheiser, that a high manganese content in the charge would decrease the rate of carbon-drop finds no support in the diagram.

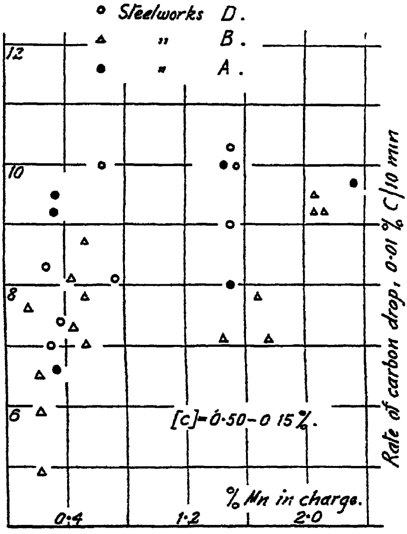

FIG. 14.

In the first nine experimental heats, steel samples for oxygen determinations were taken at rather short time intervals. One and the same rule seems to apply for these nine heats, viz., that the oxygen content of the steel increases almost linearly with time towards the end of the heat, see Fig. 1–9. The oxygen values lie rather close to straight lines: the discrepancies are not greater than the errors in sampling and analysis. As will be seen from the diagrams, the linear oxygen curves have different slopes towards the end of the heat in different heats. The slope is here denoted by $d[O]/dt$.

In Fig. 15 the values of $d[O]/dt$ (carbon range 0·20 – 0·07 % C) are plotted against the FeO content of the slag (carbon = 0·07 %). These conditions were chosen because it is reasonable to assume that the reactions have reached a "steady state" towards the end of the heat. The points in the diagram are somewhat scattered. Further, they are too few for any conclusion to be drawn.

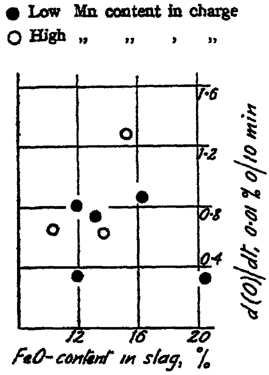

FIG. 15.

However, the FeO content of the slag is no direct measure of its oxidising power. The FeO activity in the slag may serve as such a measure. The FeO activity in basic slags of various compositions has been determined in an ingenious way by Chipman and co-workers recently [20] [21] [22] [23] (Fig. 16). In Fig. 17 the $\frac{d[O]}{dt}$ values for the experimental heats (carbon range 0·20 — 0·07 % C) are plotted against the FeO activity in the slags (carbon = 0·07 %) as obtained from Fig. 16. The scattering of the points is now smaller than in Fig. 15, but is still too large for definite conclusions to be drawn.

From Fig. 15 and 17 it may be concluded that there is no simple relationship between slag composition and the quantity $d[O]/dt$.

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[20] Chipman and Fetters, *Trans. Amer. Soc. Met.*, 1941, **29**, 953.

[21] Chipman, *Trans. Amer. Soc. Met.*, 1942, **30**, 817.

[22] Taylor and Chipman, *Trans. Amer. Soc. Met.*, 1943, **154**, 228.

[23] Winkler and Chipman, *Met. Tech.*, 1946, **13**, No. 3, Tech. Publ., 1987.

Fig. 18, showing the rate of carbon-drop (carbon range 0·20 — 0·07 %) plotted against d[O]/d*t* (same carbon range), may be of some interest in this connection. There seems to be a linear relationship between the rate of carbon-drop at low carbon contents and the rate with which the oxygen content of the bath increases. The diagram ought not, however, to be interpreted as if the quantity d[O]/d*t* determined the rate of carbon-drop. This is illustrated by the following example.

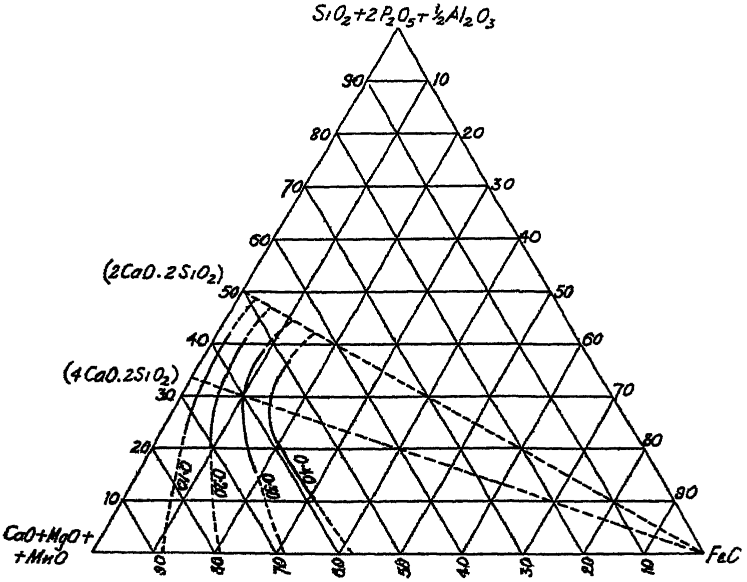

FIG. 16.—FeO-activities in basic slags according to Winkler and Chipman[23]

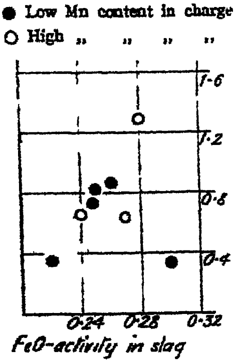

FIG. 17.

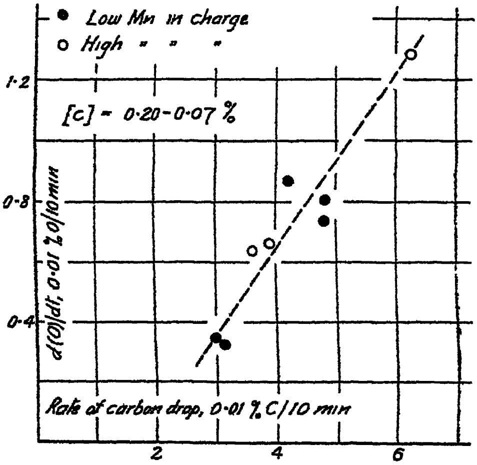

FIG. 18.

To maintain a rate of carbon-drop of 0·04 % C per 10 min. at a constant oxygen content in the bath, it is required to supply the bath with an amount of oxygen equal to *ca.* 0·053 % O per 10 min. This oxygen reacts with the carbon and is evolved as CO. At the same time the oxygen content of the bath is increased by *ca.* 0·006 % O per 10 min. The total amount of oxygen supplied to the bath is therefore *ca.* 0·059 % O per 10 min. Because it is only about one-tenth of this amount that remains in the steel, it seems difficult to imagine that this comparatively small amount, represented by d[O]/d*t* in the diagram could be the primary factor governing the magnitude of the rate of carbon-drop. It seems likely that other factors are more important, such as the prerequisites for carbon monoxide evolution and the capacity of the slag for transfering oxygen to the bath.

The results concerning the rate of carbon-drop can be summarised thus. In the various heats the rate of carbon-drop is different. There is no simple relationship between rate of carbon-drop and slag composition. A linear relationship exists between the rate of carbon-drop and the quantity of d[O]/d*t*.

The results are in agreement with the theory for the carbon reaction developed in the investigations mentioned,[10, 12, 13, 14, 16, 17, 18, 19] the main features of which are as follows.

1. The carbon reaction is a heterogeneous one. Its rate is governed by the slowest of the component processes of which it is composed. The slowest of these processes is the formation of the CO bubbles, because of which surface tension becomes a factor of first importance.

2. Hence, the rate of the carbon reaction is also governed by factors other than the concentrations of carbon and oxygen in the steel bath. The law of mass action in its simple form cannot be applied to compute the rate of the reaction [24] as was done by Schenck [25] about 15 years ago and by others until recently.

3. It is probable that the condition of the hearth surface is important for the carbon reaction, for this condition affects bubble formation, which takes place at the furnace bottom.

Summary

Thirty-six experimental heats, made in different melting shops, were studied in some detail. A new method was developed of taking steel bath samples, suited for oxygen-content determinations. The method employed gives reproducible results.

The carbon content of the bath is the factor which has the greatest influence upon the oxygen content during the refining period. The values of the product [C] × [O] are rather scattered at higher carbon contents but approach the equilibrium value at lower carbon contents. The results are in general agreement with those published by Brower and Larsen recently.

The influence of manganese upon the oxygen content of the bath and upon the carbon reaction was studied. It was found that the manganese content of the charge, which varied between 0·15 and 2·3 % Mn, has no influence upon the oxygen content of the bath and upon the rate of carbon drop. The results contradict those reported before the war by Bardenheuer and Thanheiser. Their conclusions seem to be based upon a different interpretation of the affinity between manganese and oxygen than that prevailing at present.

Surahammar,
Sweden.

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[24] Kalling, *Jernkont. Ann.*, 1935, **119**, 248 (review of Schenck's book[25]).

[25] Schenck, *Physikalische Chemie der Eisenhuttenprozesse*, Vol. 2 (Berlin, 1934).

THE PHYSICAL CHEMISTRY OF SULPHUR REMOVAL IN STEEL MAKING

By P. T. Carter

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Attempts to explain the removal of sulphur in steel making have been so numerous and varied in recent metallurgical literature that it would seem that every possible avenue of approach to this problem must have been covered, and that any further contribution must be superfluous. Even so, the most important recent contributions to the subject, while agreeing as to general conclusions, have been presented in manners so different that it is difficult to see any connection between their fundamental arguments used in reaching these conclusions. It is hoped that this paper will, in part, fill this gap. It is proposed to deal only with slag–metal relationships, although it is recognised that sulphur transfer to and from the gas can take place, and that conditions favourable for loss of sulphur from the slag to the gas phase may not be favourable for removal of sulphur from the metal to the slag.

Efforts to apply physico-chemical laws to slag–metal relationships using total concentrations of the reactants failed when applied to wide ranges of slag and metal compositions, and attempts were therefore made to make some arbitrary assessment of the free concentrations of slag components to be used instead of total concentrations for the calculation of equilibrium constants, assuming certain compounds to be formed in the slag.

A difficulty when applying these laws to the distribution of sulphur has been a lack of knowledge of the state of combination of the sulphur in both the metal and slag. Chipman[1] has indicated from a study of the atomic diameter and internal pressure of elements found in steel that it is improbable that elementary sulphur exists in steel and that it probably occurs combined as a sulphide (or possibly as sulphide ions).

Assuming that both iron and manganese may exist in liquid steel as sulphide, and that saturation with sulphide is not approached, then in the reaction

$$\text{FeS} + \text{Mn} \rightleftharpoons \text{Fe} + \text{MnS}.$$

$$K'_{\text{MnS}} = \frac{[\text{MnS}]\,[\text{Fe}]}{[\text{FeS}]\,[\text{Mn}]} \quad . \quad . \quad . \quad . \quad (1)$$

(Throughout this paper activities or concentrations in the metal are indicated by square brackets, in the slag by round brackets.)

There are no direct thermodynamic data for this reaction in liquid steel but Britzke, Kapustinsky and Wesselowsky[2] [3] have measured the dissociation pressures of solid iron sulphide and manganese sulphide by reduction experiments for temperatures up to 1270° c. They give

$$\text{FeS} \rightleftharpoons \text{Fe} + \tfrac{1}{2}\,\text{S}_2$$

$$\log p_{\text{S}_2} = \frac{-14{,}350}{T} + 5{\cdot}80.$$

$$\text{MnS} \rightleftharpoons \text{Mn} + \tfrac{1}{2}\,\text{S}_2$$

$$\log p_{\text{S}_2} = \frac{-25{,}970}{T} + 9{\cdot}15.$$

Hence for

$$\text{FeS} - \text{Mn} \rightleftharpoons \text{Fe} + \text{MnS (at } 1270^\circ \text{ c.)}$$

$$K'_{\text{MnS}} = 26{\cdot}7.$$

Chipman and Ta Li[4] have shown that the data of Britzke and Kapustinsky for the reaction

$$\text{FeS} + \text{H}_2 \rightleftharpoons \text{Fe} + \text{H}_2\text{S}$$

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[1] Chipman, *Trans. Amer. Soc. Met.*, 1942, **30**, 817.

[2] Britzke and Kapustinsky, *Z. anorg. Chem.*, 1930, **194**, 323.

[3] Britzke, Kapustinsky and Wesselowsky, *Z. anorg. Chem.*, 1933, **213**, 67.

[4] Chipman and Ta Li, *Trans. Amer. Soc. Met.*, 1937, **25**, 433.

yield an equilibrium constant which compares favourably with that from their own experiments using liquid steel. It follows that

$$K_{\mathrm{MnS}} = \frac{[\mathrm{MnS}]}{[\mathrm{FeS}]\,[\%\ \mathrm{Mn}]} = 0{\cdot}267$$

for steels containing low percentages of manganese should give a rough indication of the equilibrium existing in liquid steel. McCance [5] has shown that for average steel compositions at 1600° c., this corresponds to only 5–10 % of the sulphur present as manganese sulphide.

The partition of sulphur from metal to slag will be governed by the partition coefficients of iron sulphide and manganese sulphide, L_{FeS} and L_{MnS}

where
$$L_{\mathrm{FeS}} = \frac{(\mathrm{FeS})}{[\mathrm{FeS}]}$$

$$L_{\mathrm{MnS}} = \frac{(\mathrm{MnS})}{[\mathrm{MnS}]}.$$

Meyer and Schulte [6] have examined the equilibrium between pure sulphide slags and iron containing manganese at temperatures in the neighbourhood of 1600° c. If the value for K_{MnS} obtained above, namely 0·267, be applied to their distributions, it is found that

$$\frac{L_{\mathrm{MnS}}}{L_{\mathrm{FeS}}} = \sim 700 \text{ (for sulphide slags).}$$

Bardenheuer and Geller [7] found L_{FeS} to be 3·6 at 1600° c. when using almost pure ferrous oxide slags, and expressing sulphur in metal and slag as weight percentages. This would give a value of about 2500 for L_{MnS}. This does not agree with the value of about 300 computed by McCance from the data of Meyer and Schulte or a value of 200–300 calculated from the experiments of Bardenheuer and Geller using ferrous oxide-manganese oxide slags, and suggests that the value of $K_{\mathrm{MnS}} = 0{\cdot}267$ is too low. In the presence of other slag constituents such as lime, silica, etc., the above partition coefficients will not apply accurately if the molten slag does not behave as an ideal solution, unless activity in the slag be substituted for concentration.

It is known [8] that sulphides and silicates are only partially miscible but the work of McCaffery and Oesterle [9] has shown that over 30 % manganese sulphide can dissolve in lime–silica–alumina slags. (It is not likely that the manganese sulphide remains as such.) This large solubility of sulphides has been confirmed for calcium silicates containing iron oxide. In comparison, the percentages of sulphides in steel-making slags are very small, and the effect of partial miscibility in lowering L_{MnS} and L_{FeS} (i.e., reducing the solubility in the slag layer) should be small.

If the older classical conception of slag constitution is adopted, in which the slag components are partly combined to form compounds, whose dissociation is governed by the law of mass action, then the following chain of reactions would be expected to occur when the metal is covered by a basic slag.

[5] McCance, *Symposium on Steelmaking* (Iron and Steel Inst., 1938), 331.

[6] Meyer and Schulte, *Archiv. Eisenhütten.*, 1934, **8**, 187.

[7] Bardenheuer and Geller, *Mitt Kaiser-Wilhelm Inst. Eisenforsch.*, 1934, **16** (7), 77.

[8] Schenck, *The Physical Chemistry of Steelmaking* (British Iron and Steel Research Association, 1945), 297.

[9] McCaffery and Oesterle, *Trans. Amer. Inst. Min. Met. Eng.*, 1923, **79**, 606.

In the metal (*a*) $FeS - Mn \rightleftharpoons Fe + MnS$.

At the interface (*b*) $\underset{\text{metal}}{FeS} \rightleftharpoons \underset{\text{slag}}{FeS}$

(*c*) $\underset{\text{metal}}{MnS} \rightleftharpoons \underset{\text{slag.}}{MnS}$

In the slag (*d*) $CaO + FeS \rightleftharpoons CaS + FeO$

$$K_1 = \frac{(CaS)\ (FeO)}{(CaO)\ (FeS)} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$\Delta G^\circ = -8900 + 3{\cdot}05\,T$$

$$K_1 = 2{\cdot}36 \text{ at } 1600^\circ \text{ c.}$$

(This neglects the heat of solution of calcium oxide and calcium sulphide and it is probable that K_1 is a little higher.)

(*e*) $CaO + MnS \rightleftharpoons CaS + MnO$.

$$K_2 = \frac{(CaS)\ (MnO)}{(CaO)\ (MnS)} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$\Delta G^\circ = -10{,}000 + 0{\cdot}30T$$

$$K_2 = 12{\cdot}6 \text{ at } 1600^\circ \text{ c.}$$

(again, only an approximate figure.)

These constants indicate that practically all the sulphur in basic steel-making slags is present as calcium sulphide, and hence the possible formation of manganese sulphide in the metal can have no bearing on the final equilibrium distribution of sulphur, although it may affect the speed at which equilibrium is attained, especially if the partition at the slag-metal interface is the slowest reaction in the above chain.

According to the theory based on reactions (*d*) and (*e*), manganese may affect the distribution indirectly by its effect on the ferrous oxide content of the slag. If reactions (*d*) and (*e*) are combined

$$\frac{[FeS] + [MnS]}{(CaS)} = \frac{1}{(CaO)}\left(\frac{(FeO)}{K_1 \,.\, L_{FeS}} + \frac{(MnO)}{K_2 \,.\, L_{MnS}}\right) \quad . \quad . \quad (4)$$

In the well-known reaction :

$$FeO + Mn \rightleftharpoons Fe + MnO$$

$$K_{Mn} = \frac{(MnO)}{(FeO)\ [Mn]} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Eqn. (4) may now be written as

$$\frac{[S]}{(CaS)} = \frac{0{\cdot}364\ ([FeS] + [MnS])}{(CaS)} = \frac{0{\cdot}364}{(CaO)}\left(\frac{(MnO)}{[Mn]\,K_1\,L_{FeS}\,K_{Mn}} + \frac{(MnO)}{K_2 L_{MnS}}\right) . \quad (6)$$

or as

$$\frac{[S]}{(CaS)} = \frac{1{\cdot}64\ [O]}{(CaO)}\left(\frac{L_{FeO}}{K_1\,L_{FeS}} + \frac{L_{FeO}\ K_{Mn}\ [Mn]}{K_2\ L_{MnS}}\right) \quad . \quad (7)$$

where

$$L_{FeO} = \frac{(FeO)}{[FeO]}$$

In both (6) and (7) the last term in the brackets can be neglected because of the large value of the product $K_2\ L_{MnS}$ except when manganese is high. Eqn. (7) therefore simplifies to

$$\frac{[S]\ (CaO)}{(CaS)\ [O]} = \frac{1{\cdot}64\ L_{FeO}}{K_1\ L_{FeS}} = 20{\cdot}0$$

when $K_1 = 2\cdot36$, $L_{FeO} = 1\cdot03$, $L_{FeS} = 0\cdot036$ (molar instead of weight concentrations in slag).

This value is rather higher than that calculated from some of the experimental melts of Winkler and Chipman[10] which gave values of the order of 10–15. The difference may be because of the probable low value of K_1 referred to earlier. The free lime was calculated assuming the formation of compounds as described by Winkler and Chipman, and their dissociation constant for dicalcium silicate of 0·01. This, of course, implies that in (*d*), (CaO) represents the combined concentrations of free lime, magnesia and manganese oxide, and that these oxides are equivalent in the desulphurisation action.

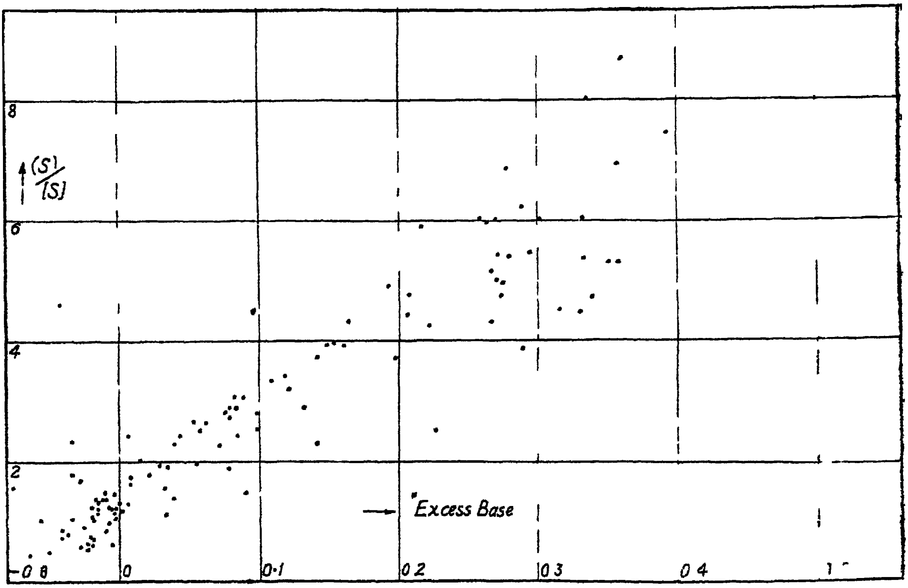

Fig. 1.

This and the following figures also contain data from Fetters and Chipman[12]

In a paper using the same experimental data, Grant and Chipman[11] have discarded desulphurisation by the above reactions (*d*) and (*e*) and attribute it to the direct partition of iron sulphide and the influence on the sulphur distribution ratio of the "excess base" of the slag. The latter was calculated assuming lime, magnesia and manganese oxide were equivalent bases and subtracting from the total base that required to form dicalcium silicate, tetracalcium phosphate, dicalcium aluminate, and if there still remained an excess of base, calcium ferrite. In many cases the excess base value was negative but Fig. 1 shows that, even including these cases, for a very wide range of slags the proportionality of excess base to sulphur distribution ratio is remarkably good, and that the ferrous oxide content of the slag apparently has no effect. Fig. 2, in which the abscissæ are Chipman and Grant's "excess base" divided by the oxygen content of the metal (little significance can be attached to the negative values), indicates that oxidising power is very closely related to basicity in nearly all their slags. Experiments where this was not the case did not conform well with the relationship shown in Fig. 1, and data of slag–metal relationships where the slag is highly basic and poorly oxidising all give much higher distribution ratios than indicated by Grant and Chipman. In extreme cases, distribution ratios of over 50 have been reported, as in the Perrin process, using a 1/1 calcium silicate slag and about 1 % iron oxide. In the desulphurisation of blast-furnace metal, ratios of over 1000 have been obtained, using blast-furnace slag to which additions of lime and fluorspar have been made

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[10] Winkler and Chipman *Trans Amer Inst. Min Met Eng* Tech Publ, 1987 (Metals Tech, 1946)

[11] Grant and Chipman, *Trans. Amer Inst. Min Met Eng*, Tech. Publ, 1988 (Metals Tech, 1946).

[12] Fetters and Chipman *Trans Amer Inst. Min Met. Eng*, 1941, **140**, 170

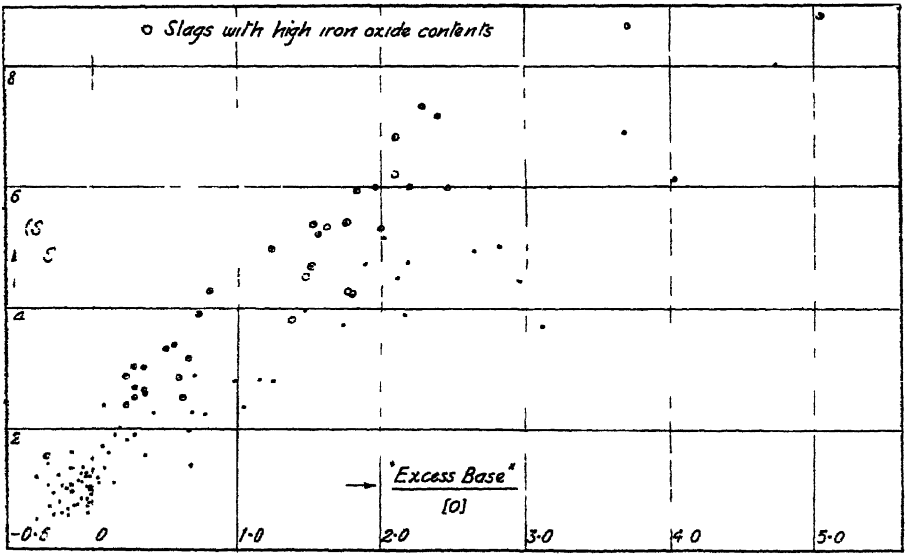

FIG. 2.

(lime, silica ratios 2–3/1). Desulphurisation in the reducing period of the electric furnace affords similar examples which make it clear that for low iron oxide slags, the concentration of iron oxide is of great importance.

Herasymenko[13] and more recently Tempkin[14] have suggested that the compounds and free basic oxides occurring in slags are completely ionised and there is considerable support for this theory from experiments on the measurement of the electrical conductivity of slags. Geller[15] investigated the electrical conductivity of iron silicate slags, and Martin and Derge[16] found considerable conductivity in blast-furnace slags, and developed a theory of slag constitution based on ionisation. Assuming that such ionic solutions behave ideally, Samarin Tempkin and Schwarzmann[17] have inerpreted the results of several workers fairly satisfactorily. According to their theory sulphur removal takes place by the partition of iron sulphide between metal and slag, their sulphur distribution coefficient K_S being given by

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[13] Herasymenko, *Trans. Faraday Soc*, 1938, **34**, 1245.

[14] Temkin, *Acta. Physicochim.*, 1945, **20**, 411.

[15] Geller, *Z. Elektrochem.*, 1940, **46**, 277.

[16] Martin and Derge, *Trans. Amer. Inst. Min. Met. Eng.*, Tech. Publ., 1569 1943

[17] Samarin, Tempkin, and Schwarzmann, *Acta Physicochim.*, 1945, **20**, 421.

$$K_S = \frac{(a_{FeS})}{[a_{FeS}]} = \frac{(a_{Fe^{++}})\,(a_{S^{--}})}{[a_{FeS}]}$$

from which is derived

$$K_S = K_O \frac{(a_{S^{--}})\,[O]}{(a_{O^{--}})\,[S]} = K_O \frac{(n_{S^{--}})\,[O]}{(n_{O^{--}})\,[S]}$$

where K_O is the corresponding distribution coefficient for oxygen, and $(n_{S^{--}})$ and $(n_{O^{--}})$ are the number of g.-ions of sulphide ions and oxide ions in the slag respectively. Where no acid constituents are present, $(n_{O^{--}})$ is equal to the sum of the number of g.-mol. bases present per 100 g. slag (CaO, MgO, MnO, and FeO, the latter being obtained from total iron). In the presence of silica, etc., and for sufficiently basic slags,

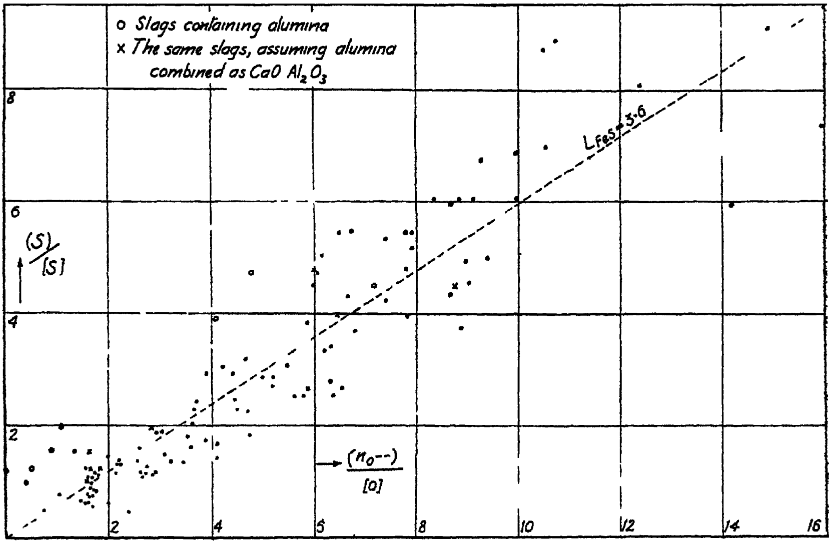

FIG 3.

$$(n_{O^{--}}) = n_{CaO} + n_{MgO} + n_{MnO} + n_{FeO} - 2n_{SiO_2} - 3n_{P_2O_5} - 3n_{Al_2O_3},$$

i.e.,

$$K_S = K_O \frac{(n_{S^{--}})\,[O]}{(n_{CaO} + n_{MgO} + n_{MnO} + n_{FeO} - 2n_{SiO_2} - 3n_{P_2O_5} - 3n_{Al_2O_3})\,[S]}\,. \quad (8)$$

The application of eqn. (8) to the experimental data of Grant and Chipman (probably the most reliable investigation of slag–metal relationships to date) is shown in Fig. 3, where $\frac{(n_{O^{--}})}{[O]}$ is plotted against $\frac{(S)}{[S]}$. The scatter of points is similar to that shown in Fig. 1 and 2. Fig. 4 shows that with one or two exceptions the constancy of K_S is good when it is remembered that the temperature factor has been neglected. Some of the data of Bardenheuer and Geller,[7] corresponding to higher sulphur contents in metal and slag, plotted on the same figure, are not so consistent.

It is clear that the distribution of sulphur between metal and slag can be interpreted with reasonable accuracy by three different methods of computation, illustrated in Fig. 1–3. Fig. 2 and 3 are both based on an equation of the type

$$\frac{(S)}{[S]} = k \frac{\Sigma (n_{MO})}{[O]} \quad . \quad . \quad . \quad . \quad (9)$$

In the older theory of slags based on molecular constitution

$$\Sigma (n_{MO}) = n_{CaO} + n_{MgO} + n_{MnO} - 2n_{SiO_2} - 4n_{P_2O_5} - 2n_{Al_2O_3} (-n_{Fe_2O_3})$$

The electrolytic ionisation theory of slags is, of course, equivalent to

$$\Sigma (n_{MO}) = n_{CaO} + n_{MgO} + n_{MnO} + n_{FeO} - 2n_{SiO_2} - 3n_{P_2O_5} - 3n_{Al_2O_3}$$

and presupposes that the compounds $2CaO . SiO_2$, $3CaO . P_2O_5$, and $3CaO . Al_2O_3$ form first and then ionise. The activity of iron oxide in calcium silicate slags containing iron oxides has been explained by Taylor and Chipman [18] only by the formation of dicalcium silicate. If further ionisation of this compound takes place, then the electrostatic attraction between the Ca^{++} and SiO_4^{----} ions formed must be such as to make the final constitution chemically indistinguishable from one in which undissociated molecules of calcium silicate are assumed to exist. The dissociation constants of calcium silicates assumed by Schenck,[8] White,[19] and Winkler and Chipman [10] to explain their experimental work, would on an ionisation theory be replaced by a factor representing the types of silicate ions formed. The apparently incomplete ionisation of compounds in slags would be analogous to the anomalous behaviour of strong electrolytes in aqueous solution.

It would appear, therefore, that to explain slag–metal relationships completely, a knowledge of the degrees of dissociation of the compounds formed in the slag is necessary. An attempt to modify the ionic interpretation represented in Fig. 3, by allowing for the dissociation of dicalcium silicate, has been made and is shown in Fig. 5. For the reaction

$$4CaO . 2SiO_2 \rightleftharpoons 2CaO . 2SiO_2 + 2\ CaO$$

$$K = \frac{(2CaO . 2SiO_2)\ (CaO)^2}{(4CaO . 2SiO_2)} = 0{\cdot}01$$

was adopted from the work of Winkler and Chipman. A chart was constructed similar to those of Schenck [8] for the determination of the free base, i.e., (CaO). In accord with Winkler and Chipman, tetracalcium phosphate was assumed the stable phosphate, and lime, magnesia, and manganese oxide as equivalent bases. It was observed that points corresponding to higher phosphate contents lay somewhat higher than a mean line drawn through all the points, especially at low basicities, whereas the reverse was the case with points corresponding to highly siliceous slags. These facts suggested that :—

(*a*) Too much base is being bound as phosphate and that tricalcium phosphate is the more stable compound. This is in agreement with the work of Oelsen and Maetz [20] on the $FeO—CaO—P_2O_5$ system, and is also expected from the relative values of the dissociation constants of the two compounds.

(*b*) Either the above value of the dissociation constant of dicalcium silicate is too high, or highly siliceous slags do not behave ideally. It is even possible that there is no dissociation.

The scatter of points in Fig. 5 is similar to that in previous figures and indicates that more knowledge is still required of the dissociation (or ionisation) of the compounds present in slags and the effect thereon of temperature, if slag–metal relationships are to be described more exactly.

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[18] Taylor and Chipman, *Trans. Amer. Inst. Min. Met. Eng.*, 1943, **154**, 228.

[19] White, *J. Iron Steel Inst., Carnegie Mem.*, 1938, **27**, 1.

[20] Oelsen and Maetz, *Mitt. Kaiser-Wilhelm Inst. Eisenforsch.*, 1941, **23** (12), 195.

With regard to the nature of slags, the electrolytic ionisation theory may present a more accurate physical interpretation of their behaviour and of slag–metal relationships, but it is clear that this theory is very closely related to the older concepts, which may give many a better picture of the processes taking place.

The above treatment has assumed that saturation with sulphide is never reached in the liquid steel. There has been, as yet, no indisputable evidence of the separation of a liquid sulphide phase from steels containing normal concentrations of sulphur, manganese, etc., although it has been suggested by Andrews and his co-workers [21] studying laboratory ingots, and Gregory [22] investigating segregation in ordinary ingots, that a partially miscible complex containing sulphur, phosphorus, carbon and manganese, can be formed even within this range of steel compositions.

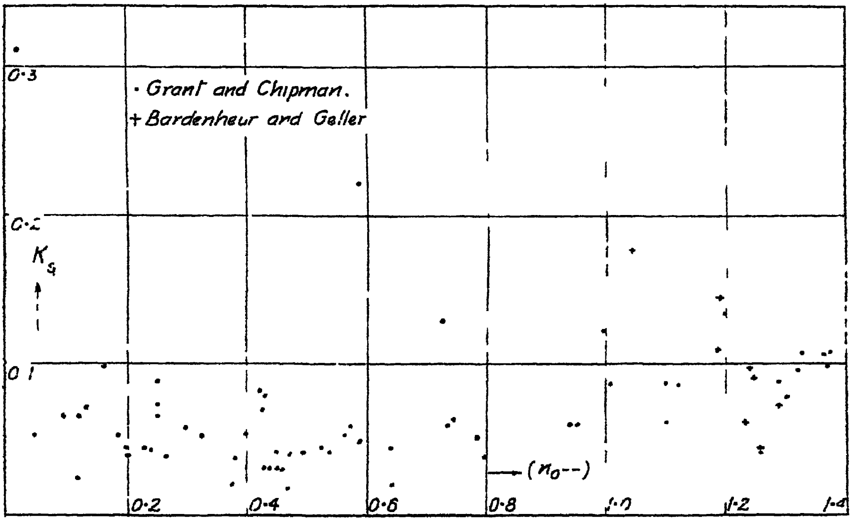

FIG. 4.

Loebe and Becker [23] have shown that iron and iron sulphide are completely miscible in the liquid state, although the flattened liquidus in the thermal equilibrium diagram indicates a tendency to separate into two liquid phases. Vogel and Baur [24] found that this separation actually occurs in the ternary system iron–manganese–sulphur. Meyer and Schulte [6] found that at 1600° C., the miscibility gap corresponded to

$$[\mathrm{Mn}]\,[\mathrm{S}] = \sim 2{\cdot}6$$

but that in the presence of carbon this product was reduced to 1·2. Similar miscibility gaps have been shown to occur in the ternary systems iron–sulphur–carbon [25] and iron–sulphur–phosphorus [26] and Ziegler [27] suggested that oxygen also may cause the formation of liquid conjugates. It is, however, generally believed that even the combined effect of the small amounts of these elements usually present in liquid steel cannot cause separation of liquid sulphides, and that this phenomenon is only of importance in the case of pig iron.

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[21] Andrews, Protheroe, Percival and MacDougall, *Eighth Report on the Heterogeneity of Steel Ingots* (The Iron and Steel Institute, Special Report, No. 25, 1939), 1.

[22] Gregory, *J. Iron Steel Inst.*, 1940, **141**, 263.

[23] Loebe and Becker, *Z. anorg. Chem*, 1922, **77**, 301.

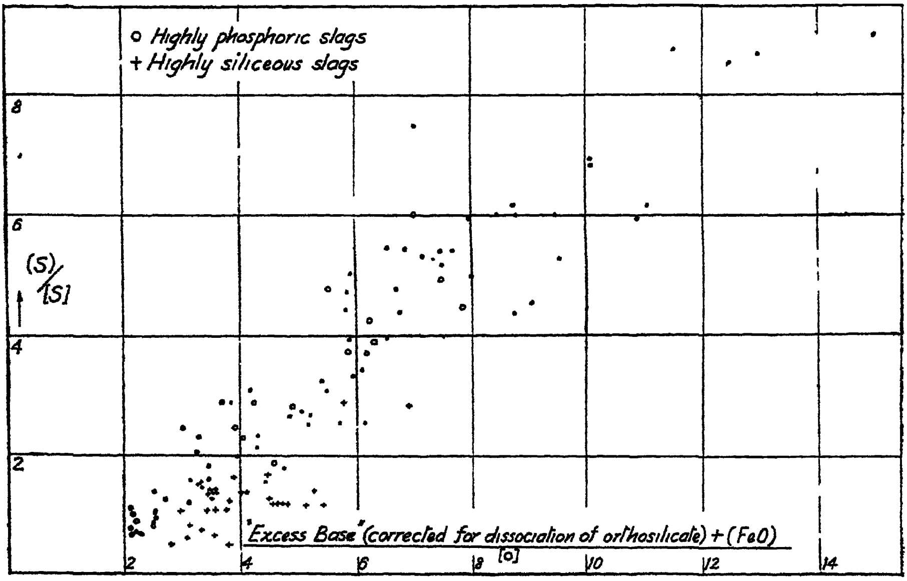
[24] Vogel and Baur, *Archiv Eisenhutten.*, 1932–33, **6**, 495.

[25] Vogel and Ritzau, *Archiv Eisenhütten*, 1930–31, **4**, 549

[26] Vogel and deVries, *Archiv Eisenhutten.*, 1930–31, **4**, 613

[27] Ziegler, *Rev. Métall.*, 1909, **6**, 459.

Partition of sulphur to the slag can take place even though the steel is not saturated, as has been described above. The presence of elements like manganese, carbon, phosphorus, etc., which decrease the solubility of sulphur in iron, should therefore increase the activity of sulphur in the liquid iron phase and increase its tendency to separate into the slag phase. The effect, though small at ordinary concentrations, will increase as compositions corresponding to those on the miscibility gap boundary are approached.



Conclusions

The experimental data which have been examined above show that sulphur distribution is best explained by a relationship of the form indicated in eqn. (9). The data also show that CaO, MgO, MnO, and FeO in the free state can all desulphurise molten iron. It appears probable that their desulphurising powers are equal. When these oxides are combined with acidic oxides to form compounds, the desulphurising power is correspondingly reduced. The states of combination best fitted to the data are $2MO . SiO_2$ (or $4MO . 2SiO_2$), which is either undissociated or only slightly dissociated, $3MO . P_2O_5$, $MO . Al_2O_3$, and $MO . Fe_2O_3$, except perhaps in the case of the less basic slags, when compounds of a more acidic nature will begin to appear. Manganese in the metal can have no effect on the final equilibrium distribution, except in so far as it may increase the activity of the sulphur in the metal phase.

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Prof. E. A. Guggenheim (*Reading*) said : Dr. Richardson has given us an illuminating and instructive survey of what is known of liquid slags. My only criticism is of his diffidence. While in complete agreement with him on fundamental matters, I should in places have expressed myself more boldly. For example, Dr. Richardson says : "Our knowledge of the structure of slag compounds in the liquid state is far less satisfactory than in the solid." Actually his survey shows that this knowledge is not at all unsatisfactory and in my opinion many of the unanswered questions are unanswered and will remain so because they are silly questions. I refer particularly to the question whether the liquid slag is composed of molecules or ions. I propose to analyse this question rather more deeply than has been done hitherto.

We know in considerable detail the structures of solid slags and we know that these structures are assumed because they are the most stable. We also know that liquid slags are constituted from the same atoms as solid slags and that these atoms are subject to the same fundamental laws. Finally, as stressed by Dr. Richardson, the entropy of melting per atom is notably small. This shows that the structure of the liquid slag must be very similar to that of the solid. I assert that this is knowledge, not speculation. The essential characteristic of the liquid, differentiating it from the solid, is its greater disorder. We are admittedly ignorant of the finer details of this disorder, but that is not a serious gap in our knowledge.

This state of knowledge, which seems to me quite satisfactory, becomes obscured when people begin complicating the description by introducing the irrelevant words "molecules" and "ions," having apparently forgotten what these words mean. I should like to remind them.

A molecule is the unit which moves about more or less independently in a gas. Measurements of the density of a gas determine the number of molecules per unit volume and so, in the case of a single gas, the formula of the molecule. In highly dilute solutions, whether liquid or solid, measurements of vapour pressures, freezing point, E.M.F. and the like determine the number per unit volume of solute molecules, that is to say of solute units more or less independent of one another. No direct information is given as to what these units are. In other words the extent of solvation is completely undetermined. In mixtures other than highly dilute solutions, the word molecule has no clear meaning and is better not used. (In the case of organic substances the molecule is recognizable by X-ray studies in the crystal and it is reasonable to assume its persistence in the liquid. This is, however, irrelevant to the kind of inorganic substances with which we are here concerned.)

So much for molecules. As for ions, the name "ion" was introduced by Faraday to denote the part of an electrolyte which moves in an electric field. If we are to be faithful to the terminology of our patron, then since a slag is a poor conductor of electricity it can contain but few ions. However, the meaning of the word "ion" has become distorted, I think mainly by crystallographers, to mean an electrically charged particle ; they speak of "free ions," meaning "ions" in Faraday's sense, and of "bound ions." They also say that a crystal of potassium chloride is composed of K^+ and Cl^- ions. It is well known that the energy of formation of the several alkali halide crystals can be accounted for by the use of Born's cycle. In making the balance sheet there are important terms representing the mutual polarizations of the cations and anions. In other words, in the crystal the potassium ion has to a large extent drawn back to itself the negative charge from the chloride ion. In fact according to Pauling, the distribution of electrons in a crystal such as KCl is such that the "effective charges" on the potassium and chloride ions are nearer to zero than to unity. The only correct description is that which specifies the positions of the atomic nuclei and the average positions of the electrons binding them together. The common statement that a KCl crystal is composed of K^+ and Cl^- ions is, therefore, overdetailed and unnecessarily misleading. What I have said of alkali halides is *a fortiori* applicable to oxides and slags.

Let us now apply these considerations to the iron oxide mixture wüstite discussed by Dr. Richardson. I propose to use the old notation $Fe^{\cdot\cdot}$ to denote an iron atom in a ferrous compound and $Fe^{\cdot\cdot\cdot}$ to denote an iron atom in a ferric compound in contrast to the symbols Fe^{++}, Fe^{+++} denoting iron atoms which have lost two and three electrons respectively. I shall likewise denote a bivalent oxygen atom by O''. Dr. Richardson's review of the experimental data proves, if proof is needed, that the equilibrium conditions can be simply interpreted in terms of the process

$$Fe^{\cdot\cdot} + \tfrac{1}{2}CO_2 \rightleftharpoons Fe^{\cdot\cdot\cdot} + \tfrac{1}{2}CO + \tfrac{1}{2}O''.$$

The essential point is that on both sides of this equation there are more or less independent reacting units each containing a *single* Fe atom. The questions to what extent these atoms are electrically charged and to what extent they are bound to oxygen are ill-defined and so not worth consideration.

Dr. J. S. Anderson (*Harwell*) (*communicated*) : Prof. Guggenheim rightly draws attention to the need to examine critically our use of the term " ion " as applied to solid compounds and the melts derived from them. The classification of such structures as " ionic " or " covalent " in constitution is certainly arbitrary, rather than clear cut. At the same time, it may be worth noticing the following points.

(i) The so-called ionic crystals do, in fact, display electrolytic conductivity at elevated temperatures. Current is transported by the migration of charged atoms, which are therefore " ions " in Faraday's original sense. It is, however, quite usual to find that conduction is *unipolar*, the transport number of one species (usually the cation, as in NaCl at moderate temperatures, AgCl, CuI) being unity. We must then conclude that the stationary species bears an equal and opposite charge, so that the structure can fairly be regarded as built up from charged atoms, to which the term " ion " is now attached by common usage. The *mobility* of these charged atoms—which may (e.g., in CuI at its melting point) exceed that of ions in the liquid state—depends on kinetic and geometrical factors, not generic factors.

(ii) In their precise determination of the electron density distribution in typical crystal structures, Grimm and Peters (1939) showed that in NaCl the localised electron clouds corresponded with the electron numbers of the Na^+ and Cl^- ions, and that the electron density distribution between atoms falls practically to zero. Any covalent contribution to binding forces can, in this instance, be at the most extremely small.

(iii) The ionic description of a binary compound is one limiting approximation only. A collective electron model, which overweights covalent character, is an alternative approximation. Where two elements differ widely in electronegativity (e.g., the fluorides and oxides of the metals), the ionic model is usually a good approximation. In such a series as the compounds MO, MS, MSe, MTe, of some bivalent metal, where the difference in electronegativity decreases progressively, it becomes decreasingly permissible to describe the compounds in terms of the ionic model. Some collective electron model, which takes account of the increasingly important polarisation forces, becomes more applicable. It is in this connection that Prof. Guggenheim's criticism is particularly justified.

Dr. J. O'M. Bockris (*London*) (*communicated*) : The following observations are relevant to Prof. Guggenheim's remarks on the constitution of liquid slags and connected matters.

Prof. Guggenheim states that the structure of a liquid slag is similar to that of the solid and that this state of knowledge is satisfactory. This statement concerns a well-known fact (the most direct basis for which concerns the X-ray analysis of silicates [1]) and many liquids have the general characteristic referred to ; this state of knowledge is a beginning rather than an end of the study of the structure of liquids. This can be appreciated from most accounts of the structure of liquids.[2]

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[1] Parmalee, Clark and Badger, *J. Soc. Glass Tech.*, 1929, 13, 285.

[2] Fowler and Guggenheim. *Statistical Thermodynamics* (Cambridge, 1939), 319.

The significance at present attached to the word ion is "an atom or group of atoms, which possesses one or more net positive or negative charges."[3] Prof Guggenheim's historical method of taking the definition from that given by Faraday is hardly of general applicability as can be realised by consideration of the similar special case of Dalton's definition of an atom as an indivisible particle. Conclusions based upon definitions of an ion given by Prof. Guggenheim may not, therefore, be applied to work in which the usually accepted definition is (somewhat excusably) tacitly adopted.

Prof. Guggenheim's statement that a slag is a poor conductor of electricity does not include a reference substance so that its precise meaning is not clear. Compared with the electrical conductivity which other ionic conductors have, or would be expected to have, under similar conditions the slags hitherto examined are among the highest ionic conductors known. Prof. Guggenheim's conclusion that, on the grounds of their poor conduction, slags have few ions appears somewhat unjustified.

Prof. Guggenheim implies that quantitative success of the ionic model for certain alkali halides is connected with the fact that the mutual polarisabilities of cations and anions are taken into account, and that this allows for his contention that, in, say, KCl, the K^- ion has to a large extent drawn back to itself the negative charge of the Cl^- ion. These contentions are in marked disagreement with the fact that, taking the mutual ionic polarisabilities into account, this makes less than 10 % difference to the calculated value for the dissociation energies of these substances.[4]

Dr. J. White (*Sheffield*) (*communicated*) : Several speakers have been at pains to explain what is now the accepted view of the ionic structure of liquid silicates. This is now, of course, well known to all workers in this field and is not at issue With regard to the use of "molecular" models it seems possible that the use of such molecular groupings of ions and of mass-action dissociation constants may be simply a convenient means of expressing the effects of the short-range order, which, as has been pointed out, almost certainly exists in liquid oxide melts. The assumption of "molecules" based on the known compositions of the solid phases would appear to fulfil the stoichiometrical requirements of such order, while the form of the constants used is such that they can probably be regarded as expressing the probability of the various types of order postulated arising in the liquid. Thus in a solution of atoms or molecules of A and B the probability of finding A–B "bonds" formed is, in the disordered state, proportional to the product ab (where a and b are the molecular concentrations) and is a maximum at the composition AB, i.e., when $a = b$. (Compare, for example, the probability of finding A–B "bonds" in a disordered solid solution of A and B.) If groupings involving two of A to one of B are involved then the probability is proportional to a^2b and is a maximum at the composition A_2B and so on. At high degrees of order such as occur in ordered solids, these relationships cease to hold and are replaced by additive relations due to the geometrical requirements of the particular type of order involved. In the liquid state, however, where the degree of order is presumably relatively low, they can probably be expected to hold to a fair degree of approximation. The order envisaged is not, of course, simply the result of complete randomness, when the probability of getting any particular type of ordered grouping is very low, but is one which is favoured due to the fact that it is accompanied by a free-energy change.

As an example, the curve showing the relation between the ferric and ferrous ion contents of liquid iron oxide and oxygen pressure at 1600° c., as shown in Dr. Richardson's Fig. 5, can be considered. He considers that a slope of 4/1 is to be expected with both liquid and solid oxides. Dr. Hoar, on the other hand, has pointed out that for the solid oxide at least the formation of vacant sites must be allowed for, a treatment which has proved satisfactory for the case of cuprous oxide, and the predicted slope at low ferric ion contents then becomes 6/1. Neither is, however, necessarily correct since if ordering occurs allowance must be made for the free-energy change associated with such ordering. In the liquid state at least, some ordering appears likely as pointed out by Dr. Richardson and is formally allowed for in the molecular treatment by writing

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[3] McInnes, *Principles of Electrochemistry* (New York, 1939), 17. Starling, *Electricity and Magnetism* (London, 1943), 170. Glasstone, *Electrochemistry of Solutions* (London, 1945), 15.

[4] Körtum, *Lehrbuch der Elektrochemie* (Leipzig, 1948).

$$\frac{(FeO)(Fe_2O_3)}{(Fe_3O_4)} = \text{constant}.$$

Taking $K_F = 0{\cdot}132$ and $K_{FF} = 0{\cdot}198$ (see our paper in this Discussion, these values being amended as suggested there to give better agreement with Chipman's data) the curve shown in Fig. 1 is obtained. At low ferric ion contents the slope of this curve is appreciably lower than that predicted by Dr. Richardson, but changes direction as the composition of Fe_3O_4 is approached. This is consistent with the view that ordering occurs. Further a maximum concentration of "Fe_3O_4" is predicted at the composition of the compound corresponding to maximum ordering at this composition as is to be expected. The curve shown deviates somewhat from the present writer's experimental points with decreasing oxygen pressure, but this is in agreement with his previously expressed opinion [5] that pick-up of iron by the platinum crucibles was probably insufficiently corrected for, particularly at the lower oxygen pressures.

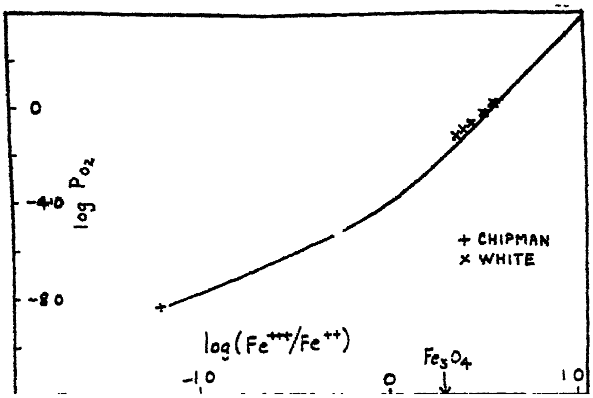

FIG. 1.

Dr. T. P. Hoar (*Cambridge*) (*communicated*): I should like to express agreement with the model proposed in Richardson's paper for the structure of wüstite, which we arrived at after a fruitful discussion. The view that ferric ions and vacant cation sites may be regarded as partially associated, to an extent depending on temperature, may well be applicable to other similar cases. It is fair to add, however, that the *increase* of the gradient of the $\log p_{CO_2}/p_{CO}$ against $\log [Fe^{+++}]/[Fe^{++}]$ plot with increasing $[Fe^{+++}]$ indicates *decreasing* association if we assume ideality; the departure from ideality must therefore be rather great if, as is necessary from first principles, association in reality increases with increase of $[Fe^{+++}]$.

Dr. J. O'M. Bockris (*London*) (*partly communicated*): Whilst agreeing with the trend of Dr. Richardson's conclusions, drawn from certain indirect evidence, on the structure of binary silicate melts, I think it is worth paying attention to how he gets them. The author states that "it is therefore proposed to adopt a thermodynamic approach" (to the elucidation of the nature of slags), "relying on the concept of chemical potentials and activities ... tempered by ... knowledge of ... structures of solid slag components." An approach to the nature (and hence presumably structure) of a phase from the viewpoint of chemical potential and activities is likely to be of strictly limited use: thermodynamic data on systems in equilibrium can in principle lead to no information concerning the structure of the phase concerned. A proposed structure (based upon some other approaches) can be shown not to contradict the thermodynamic data but, as is apparent particularly from the literature of such studies with silicate melts, they are not often diagnostic of a certain structure (cf. their varied use in support of entities such as $Mg_2Al_4Si_5O_{18}$; $Ca_8Al_2Si_2O_{15}$, etc.).[6] The only definite thermodynamic evidence on structure in Dr. Richardson's paper is that on the entropy of fusion of sodium silicate. (Prof. Rey's calculations of the activity of silica in $MO–SiO_2$ mixtures, formally uncriticisable, may be also useful in some way, but this is certainly not in the direction of attaining to a detailed model of these systems, which, it is submitted, is the first matter not only of academic interest, but also of technological expediency.)

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[5] hite, *J. Iron Steel Inst.*, 1943, **2**, 579.

Dr. Richardson's dismissal of the results of Samarin, Tempkin and Schwarzmann's work[7] on certain equilibria between slags and metal as "almost certainly fortuitous" is misleading. The Russian authors' formulation, following the original work of Herasymenko,[8] corresponds to an ideal version of the model which is now being formed from kinetic measurements and in this way is the least inaccurate formulation of such equilibria so far reported. Kheinemann[9] tried to estimate in a very rough way the effect of departures from ideality on Tempkin's equations[10] and a development of these on a proper statistical mechanical basis, is surely the direction in which slag-metal equilibrium studies should proceed.

It seems that Prof. Rey has used some unusual ionic radii to reach his conclusion that the non-oxygen attraction * sequence does not accord well with the order of the liquidus lines in the systems $MO-SiO_2$. Accepting the order stated in Rey's paper, the systems and their appropriate ion-oxygen attractions[11] are as follows ($-SiO_2$ understood in each case): Cs_2O, 0·22; Rb_2O, 0·24; K_2O, 0·27; Na_2O, 0·35; Li_2O, 0·45; BaO, 0·51; SrO, 0·59; CaO, 0·69; MnO, 0·81; ZnO, 0·91; MgO, 0·95; FeO, 0·87. The sequence of the ion-oxygen attractions is therefore perfectly satisfactory except for FeO, the displacement of which is doubtless due to the presence of Fe^{3-} ions (ion-oxygen attraction 1·57) in $FeO–SiO_2$ melts. These facts support the ionic model of the silicate melts.

Mr. J. A. S. Mowat (*Cambridge*) said: I am surprised that Dr. Richardson should have omitted from his list of methods of investigating the nature of slags, the classical methods of mineralogy and petrology—especially the examination of thin sections by means of the petrographic microscope.

Recent papers by Agrell[12] and Mason[13] are devoted to the investigation of slags by these methods. Prof. Tilley of the Department of Mineralogy in Cambridge, who has made a special study of these problems, has recently identified a new mineral—"bredigite"—in spiegeleisen slags.[14] Similar work is in progress in the Department of Geophysics in Cambridge. It may be argued that these methods are of value only in determining the structure of solid slags, but as pointed out elsewhere in this Discussion, the latent heats of melting of slags are small, so that the structures of the liquids cannot be very different from those of the solids. I feel, therefore, that the evidence of the nature of the compounds present in solid slags should be useful in deciding what sort of model to adopt when considering the nature of the molten slags.

As was pointed out by Mr. Metcalfe, in the case of basic open-hearth slags[15] there may be more than one phase present. A finely dispersed solid lime-rich phase, and solid nagelschmidtite, a lime-silica phosphate, co-exist with the liquid. In such cases, the petrographic microscope will reveal the existence of solid particles, whereas electrochemical methods will not.

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[6] Schenck, *Physical Chemistry of Steelmaking* (London, 1945), 324.

[7] Samarin, Tempkin and Schwarzmann, *Acta Physicochim.*, 1945, **20**, 421.

[8] Herasymenko, *Trans. Faraday Soc.*, 1934, **34**, 1245.

[9] Kheinemann, *Bull. Acad. Sci. U.R.S.S.*, 1946, **10**, 1439.

[10] Tempkin, *Acta Physicochim.*, 1945, **20**, 411.

[11] Bockris, Kitchener, Ignatowicz and Tomlinson, This Discussion.

[12] *J. Iron Steel Inst.*, 1945, No. 2.

[13] *J. Iron Steel Inst.*, 1944, No. 2.

[14] *Miner. Mag.*, March, 1948.

[15] Jay, *J. Iron Steel Inst.*, 1945, No. 1, 511.

* $\frac{ze^2}{a^2}$, where e is the electronic charge, and a is the internuclear distance between the metal ions and oxygen ions at the distance of closest approach.

Dr. Richardson (*B.I.S.R.A., London*) (*partly communicated*) : I am indebted to Dr. Hoar for drawing my attention to the way in which vacant lattice sites should be expected to occur in the equilibrium expression for the reaction between gaseous oxygen and ferrous and ferric iron in wüstite. I have amended my original treatment to include this point.

I am also grateful to Prof. Guggenheim for his constructive comments and for pointing out that so far as slag-metal equilibria are concerned it is irrelevant whether any atom or group of atoms carries a net charge or not. A knowledge of the electric properties of these melts does, however, help in developing a detailed model, and should assist in understanding detailed reaction mechanisms. Conductivity and transport experiments indicate at what boundaries shear takes place in these liquids and hence the weakest linkings in that giant molecule which is a slag. Finally the electrical properties may be of considerable importance in arc furnace processes.

With regard to Mr. Mowat's remarks on the value of the petrographic microscope, I fully agree that this is an extremely useful instrument, since it can be used to identify phases produced in slags after *cooling or quenching* in various ways, and to measure their optical properties. I feel, however, that its application is covered in my paper by my reference to the value of phase diagrams, for it is in the construction of them that the petrographic microscope is most valuable.

Dr. Bockris seems to think that my paper contains too much thermodynamics and too little direct evidence of the constitution of liquid slags. This could hardly be otherwise since at the present time most of the research on liquid slags has consisted of slag-metal equilibrium studies. Our intimate knowledge of liquid slags has to be inferred from our knowledge of the crystalline state and of solid glasses. I would agree with him that classical thermodynamics alone, and that really means the results of thermal and equilibrium measurements, cannot give an intimate picture of slag structure. This can be obtained only by collecting information derived by many methods and piecing it together, as I have in my paper. The resultant picture must, however, check with the energies and entropies obtained by thermodynamic methods, and if it fails to do so it must be wrong. The great power of the thermodynamic method is that it enables information derived from many sources to be applied quantitatively to the systems with which we are particularly concerned, and immediately reveals inconsistencies and discrepancies.

Dr. Bockris also suggests that I have dealt unfairly with the ionic representation of slag-metal equilibria. I have said that it is fortuitous that the simple ionic treatment developed by Tempkin and others fits the sulphur equilibrium between slag and metal so well. By this I mean that had they applied it to other systems than basic slags containing calcium, iron and manganese, which show very similar differences between their energies of association with oxygen and sulphur, it would not have proved satisfactory. It is not necessarily an advance, to express the equilibrium condition in terms of ions, although I agree that it is frequently more convenient. For instance, it is more convenient to express the sulphur equilibrium between iron and basic silicate slags in terms of the equation,

$$[S] + (O^{=}) = [O] + (S^{=}),$$

rather than,

$$[S] + (\text{O not attached to silicon}) = [O] + (\text{S not attached to silicon}).$$

As Prof. Guggenheim's remarks also suggest, it is more sensible and in most cases more strictly accurate, to express the equilibrium in terms of atoms or groups of atoms, and to regard the slag as one giant molecule in which certain atoms, or groups of atoms, can substitute for one another as the equilibrium conditions are changed.

In reply to Mr. Emley's query concerning the calculation of the activity coefficients of slag components directly from various ionic models for slag structure, by means of Debye-Hückel theory, I know of no attempts to do this. Since that theory deals solely with the coulombic forces between entities carrying various charges in a medium of uniform dielectric constant, it seems to me that it cannot at present take account of the effects of ion sizes and repulsive energies, or the "covalent" bonding in systems of close-packed atoms or ions. I feel that a more promising approach might come from an extension of the ideas developed by Born, Haber, Madelung and others for the energetics of ionic crystals.

Dr. P. Herasymenko (*Sheffield*) said: The contribution by Dr. Willis is a very able demonstration of the inadequacy of the two postulates frequently used in theoretical treatment of equilibria between metal and slag:

(i) the assumption of the existence of oxides and molecular compounds in slags, and

(ii) the assumption of the validity of the ideal mass-action law.

Several authors have tried to show in this Discussion that there is no fundamental difference between the theories based on ionic concepts and on the assumption of neutral oxides and their compounds. Dr. Willis proves that a formal similarity can be observed only in special cases.

In their early attempts, many metallurgists laid too much hope in the ideal mass-action law considering it as the only method capable of bringing about some theoretical order in the complexity of slag-metal reactions. This hope has not been substantiated by further researches and the ideal mass-action law has proved to be rather a Procrustean bed. Unfortunately the theories of concentrated liquid solutions are not yet sufficiently developed to be of much help in predicting the physicochemical behaviour of slags. It is questionable whether the application of Hildebrand's ideas on regular solutions to slags will be successful. A regular solution is defined as one in which the distribution and orientation of particles are completely random. Electrochemical nature of slags implies already a certain order in distribution of charged particles, and there are many other indications that ionic silicate melts possess a considerable degree of structural order which depends on the composition and is not very remote from the order of crystalline bodies. In this respect the work of Dr. Bockris and Dr. Kitchener and Messrs. Ignatowicz and Tomlinson gives an important information. Amongst many interesting results of their investigations I shall emphasise the occurrence of maxima on the curves of activation energy at certain compositions of melts studied at the Imperial College of Science and Technology.

The occurrence of maxima and sudden changes in the properties of silicate melts is a quite general phenomenon. From the analysis of the existing experimental data on viscosity and other properties, I have also come to the conclusion that the activation energy of rate processes can serve as a good indication of structural changes in silicate melts—in some cases even more sensitively than the absolute values of viscosity or conductivity. This is illustrated in Fig. 1, showing the viscosity isotherms (at 1350° c.) and the activation energies for the systems K_2O–SiO_2, Na_2O–SiO_2 and Li_2O–SiO_2 investigated by Endell and co-workers.[16] Similar maxima and abrupt changes in activation energy of viscous flow were found to occur at almost the same molar contents of silica in the systems CaO–SiO_2[17] and CaO–MgO–SiO_2.[18] Sudden breaks in the potential-composition curves were observed by Chang and Derge[19] for galvanic elements composed of graphite and silicon carbide electrodes in molten CaO–SiO_2 slags. All data indicate that profound changes take place in silicate melts when the ratio of silicon atoms to oxygen atoms exceeds certain values. Endell and Hellbrügge[16] and Preston[20] explained these changes by the existence of various types of silicate anions. Thus at high Si/O ratio, the silicate melts contain mainly particles with three-dimensional framework of silicon tetrahedra; when the Si/O ratio decreases, only two-dimensional network particles of silicon tetrahedra are able to exist in the form of rings; at still lower Si/O ratio (below about 3) the ring complexes dissolve into chains, the extreme case being the single SiO_4^{4-} ions.

This classification involves the assumption that silicon atoms (ions) possess only tetrahedral co-ordination. The assumption cannot, however, explain the behaviour of silicate melts entirely satisfactorily. The fact that an increase of temperature *alone* leads to a large decrease of the viscosity or, in other words, to the transformation of large anionic complexes into simpler particles, can be interpreted only on the assumption that "free" silicon and "free" oxygen ions are also formed in this dissociation of complexes.

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[16] Endell and Heidtkamp, *Glasstechn. Ber.* 1936, **14**, 89; Endell and Hellbrügge, *Beih. Z. Ver. D. Chem.*, 1940, Nr. 38.

[17] Rait and Hay, *J. Roy. Tech. Coll. Glasgow*, 1938, **4**, 252; Rait, McMillan and Hay, *J. Roy. Tech. Coll. Glasgow*, 1939, **4**, 449.

[18] McCaffery and others, *Trans. Amer. Inst. Min. Met. Eng.*, 1932, **100**, 64.

[19] Chang and Derge, *Trans. Amer. Inst. Min. Met. Eng.*, 1946, Tech. Pub. **2**, 101.

[20] Preston, *J. Soc. Glass. Tech.*, 1942, **26**, 82.

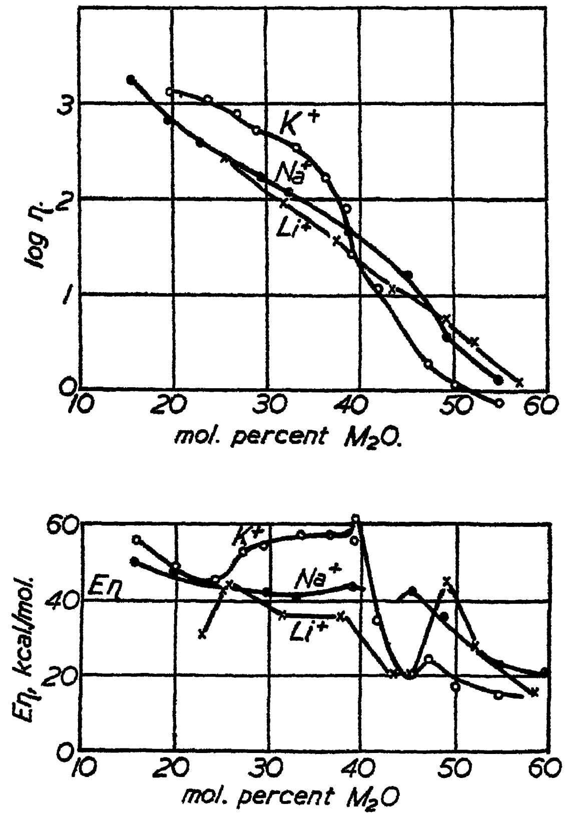

Fig. 1.—Viscosity and activation energies of flow in K_2O–SiO_2, Na_2O–SiO_2 and Li_2O–SiO_2 melts from the data of Endell and co-workers

Let us consider, for example, the reaction schemes for the thermal dissociation of a hexagonal ring-shaped anionic complex into simpler charged particles. Two of the possible schemes are indicated in Fig. 2. Almost all dissociation schemes lead to the formation of "free" silicon cations and "free" oxygen ions. By the term "free" silicon ions we understand silicon ions having a larger distance from the oxygen anions than silicon atoms in the tetrahedral complex SiO_4; this corresponds to the higher co-ordination number, probably 6, for silicon in silicate melts. The existence of free silicon and free oxygen ions in silicate melts is thus a logical necessity following from the ionic theory and from the thermal dependence of the viscosity. The silicate melts represent equilibrium mixtures of free metallic and silicon cations, free oxygen anions and various types of complex silicate anions. The proportions of different complexes in the melt will depend on the ionic environment.

Dr. Willis mentions that the correct equation for the phosphorus reaction should be:

$$2P + 5Fe^{++} + 8\,O'' = 2PO_4''' + 5Fe.$$

This equation was suggested in my paper in 1941,[21] where it was shown that the equilibrium ratio of this reaction strongly depends on the contents of calcium and oxygen ions. In our recent investigation[22] we succeeded in resolving the effects of calcium and oxygen ions: the activity of phosphate ion depends only on the content of Ca^{++} ions, whereas that of ferrous ions is influenced by oxygen ions only.

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[21] Herasymenko, *Z Elektrochem.*, 1941, **47**, 588.

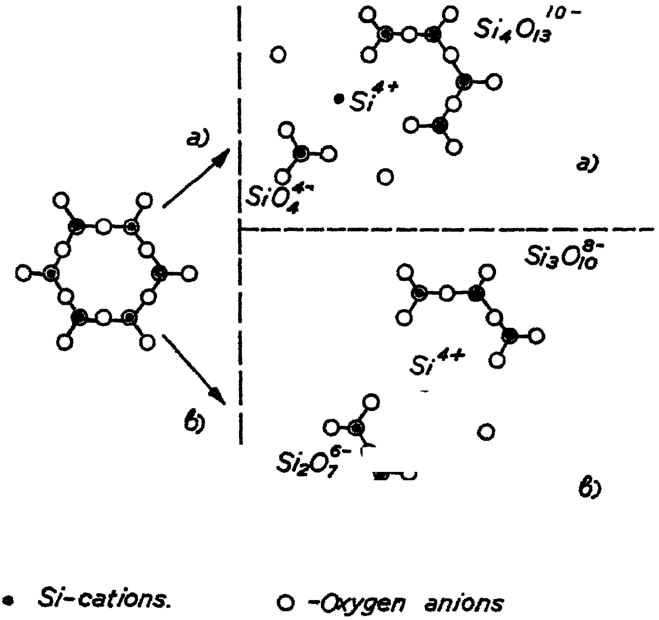

FIG. 2.—Two schemes of the thermal decomposition of a ring of silicon tetrahedra

The effect of calcium ions on the stability of phosphate ion can be explained as follows. Central (phosphorus) atom in the complex attracts oxygen atoms more powerfully when the ionic environment of the complex ion is more feeble. When the small Fe^{++}, Mn^{++}, Mg^{++} ions surrounding PO_4''' are gradually replaced by larger Ca^{++} ions which produce a weaker electrostatic field, the distance between oxygen and phosphorus atoms in the complex decreases and phosphorus is more effectively shielded.

This is probably a general phenomenon for complex oxygen-bearing anions. The electrostatic influences of environment can explain the variations in the stability and reducibility of complex ions; therefore it is necessary to assume the formation of undissociated molecules of calcium phosphate, calcium ferrite, etc.

A remark on the terminology seems to be warranted at this place. Formulæ expressing the mass-action law for metallurgical equilibria lead as a rule to values which vary with the composition of slag. It seems illogical to call them constants and I would suggest that we use instead the term "equilibrium ratio." (German workers translate the "equilibrium constant" as *Gleichgewichtskennzahl.*)

Dr. P. Gross (*Stoke Poges*) said: Dr. Herasymenko has mentioned that the application of Debye and Hückel's theory of electrolytes to slags might elucidate some points of their behaviour. According to Debye's theory, the mutual electrostatic interaction and the Brownian dispersion of the ions leads to an ion atmosphere (of opposite sign) surrounding each ion. The radius of this atmosphere is the characteristic length of Debye's theory, and its variation with the concentration for dilute solutions of ions in non-ionic media is related to the dependence of the average electrical potential of the ions, and hence of their activity coefficient, on the ionic concentration.

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[22] Herasymenko and Speight (unpublished investigation).

In sufficient dilute solutions of molten electrolytes in each other, the dissolved ions are surrounded by solvent ions of the opposite sign, and the average radius for this atmosphere (which is not essentially influenced by the thermal movement of the ions) is not dependent on the concentration but is essentially constant. The electrostatic activity coefficient is therefore constant (i e., unity), and dilute solutions of electrolytes in fused salts behave as ideal dilute solutions. It seems unlikely that consideration of the pure electrostatic interaction can contribute anything which goes further than these rather old conclusions.[23]

Dr. H. J. T. Ellingham (*London*) (*communicated*) : In view of the importance attached to the ionic constitution of slags, it would seem desirable to apply to these systems methods of investigation involving E.M.F. or decomposition voltage measurements illustrated in the paper by Rose, Davis and Ellingham (this Discussion). Measurements of E.M.F. of cells of the type, $M|slag|O_2$, where M is a metal whose ions are present in the slag and which does not displace other metals contained in it. For this purpose an effectively reversible oxygen electrode can be obtained by the use of silver as an intermediary ; oxygen is bubbled through the melt in the vicinity of a silver plate or wire or, at temperatures above the m.p. of silver, through the molten metal contained in a porous vessel dipping into the melt.[24] By such means the relative activities of certain metal ions in related types of slags might be estimated. It might also prove possible to develop the use of a sulphur gas electrode for investigating slags containing metallic sulphides.

Mr. P. T. Carter (*Glasgow*) said: The existence of completely ionised molten slags has been stressed in several of the papers presented to this Discussion. Whereas the evidence of the well-known crystalline structure of solid silicates and of the ionic conduction of molten silicates cannot be refuted, it is felt that the distinction between a slag constitution based on ions and one based on the assumption of the existence of compounds in the slag is more nominal than real. In the paper by Bockris, Kitchener, Ignatowicz and Tomlinson reference is made to the pink colour of fused $MnO–SiO_2$ mixtures up to 60 % MnO. Molten $MnO–SiO_2$ mixtures of compositions near that of rhodonite ($MnO . SiO_2$) on quenching certainly give rise to a pink glass, which can be further annealed to give pink crystalline rhodonite. Glasses obtained by quenching molten mixtures of compositions approaching that of tephroite ($2MnO . SiO_2$) show the green colour of manganous oxide, whilst in the crystalline state tephroite is almost colourless and manganous oxide is green. If the pink colour of molten rhodonite is to be attributed to the presence of manganous ions, then it must be inferred that all the manganese cannot be present as manganese ions in melts richer in MnO than $MnO . SiO_2$. It is agreed that, e.g., in molten $2 MnO . SiO_2$, the silicate tetrahedra known to be present in the solid state should still exist, but it is suggested that the electrostatic attraction between Mn^{++} and SiO_4^{4-} ions is such as to make the resultant structure equivalent to a " molecule " of Mn_2SiO_4 (further association of these " molecules " may of course occur). It has long been accepted that there is no sharp dividing line between ionic and covalent bonding and it is suggested that some intermediate type of bonding exists in this case. The electrostatic attraction of SiO^{3-} ions (the anion expected from $MnO . SiO_2$) whether single or in chains, might be expected to be less, giving rise to " $MnSiO_3$ " groupings in which the manganese ions are less closely held. They may even be completely free, thus representing true ions.

This picture is thought to apply with equal force to dicalcium silicate and tricalcium phosphate. These are two of the most important compounds found in solidified basic slags, although others have been found, e.g., merwinite ($3 CaO . MgO . 2SiO_2$) and various substituted dicalcium silicates, e.g., $CaO . MnO . SiO_2$, and one would not be surprised to find similar groupings still persisting in the liquid state. (If objection is taken to the words " compound " and " molecule," the terms " ionic compound " and " ionised molecule " may be preferred.) Recent viscosity measurements by Losana[25] support the occurrence of the compounds $2\ FeO\,.\,SiO_2$ and $2\ MnO\,.\,SiO_2$ in liquid slags. A separation of these groupings of atoms into ions would be expected to take place in the molten state under the influence of an applied electromotive force. The compounds nagelschmidtite, $7\ CaO\,.\,P_2O_5\,.\,2\ SiO_2$, and silicocarnotite, $5\ CaO\,.\,P_2O_5\,.\,SiO_2$, are actually solid solutions of Ca_2SiO_4 and $Ca_3(PO_4)_2$ and occur over a range of compositions along the Ca_2SiO_4–$Ca_3(PO_4)_2$ join (which seems to be a true binary section) in the CaO–SiO_2–P_2O_5 thermal equilibrium diagram, so that there is no need to postulate the existence of such "compounds" in the liquid state.

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[23] Gross, *Z. anorg. Chem.*, 1926, 150, 339.

[24] cf. Baur and Tobler, *Z. Elektrochem.*, 1933, 39, 169.

Willis in his paper suggests the existence of discrete PO_4^{---} ions, and on this basis represents the reaction for the removal of phosphorus as

$$2[P] + 5[Fe^{++}] + 8[O^{--}] \rightleftharpoons 2[PO_4^{---}] + 5\ Fe,$$

whence

$$K = \frac{(PO_4^{---})^2\,[Fe]^5}{[P]^2\,(Fe^{++})^5\,(O^{--})^8} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

From this it is seen that K is expressed in terms of $\frac{(P_2O_5)}{[P]}$ instead of $\frac{(P_2O_5)}{[P]^2}$, the ratio used by many recent investigators of this problem.[26] [27]

It is known that phosphorus removal does not take place, unless (PO_4^{---}) ions are removed from the sphere of action by the action of strong bases such as lime. The assumption of a specific combination between Ca^{++} and (PO_4^{---}) ions results in K being expressed in terms of $\frac{(P_2O_5)}{[P]^2}$, if the reactions are represented as follows—

In the metal, $$2P + 5O \rightleftharpoons P_2O_5 \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

At the interface, $$P_2O_5\ (\text{metal}) \rightleftharpoons P_2O_5\ (\text{slag}) \quad . \quad . \quad . \quad . \quad (b)$$

In the slag, $$P_2O_5 + 3O^{--} \rightleftharpoons 2PO_4^{---} \quad . \quad . \quad . \quad . \quad (c)$$

$$3Ca^{++} + 2PO_4^{---} \rightleftharpoons Ca_3(PO_4)_2 \quad . \quad . \quad . \quad (d)$$

Combining reactions (*a*)–(*d*)

$$K_P = \frac{(P_2O}{[P]^2\,[O]^5\,(O^{--})^3\,(Ca^{++})^3} \quad . \quad . \quad . \quad (2)$$

If reaction (*d*) were to go only to partial completion, a ratio intermediate between $\frac{(P_2O_5)}{[P]^2}$ and $\frac{(P_2O_5)}{[P]}$ would be expected, and would explain why certain workers find phosphorus distribution explained equally satisfactorily using either of these two ratios. The writer would prefer, however, to regard calcium phosphate as being essentially un-ionised in the sense indicated above. It is agreed that if relatively stable ionic complexes such as $3Ca^{++}\,.\,2PO_4^{---}$ are formed, they may not form ideal solutions, but it is felt that an equation of the general form shown by (2) governs phosphorus removal in steel making, and from such an equation the qualitative factors of importance can be deduced. (O^{--}) obviously depends on the oxygen ions which can take part in reaction (*c*). It would be expected to include all "excess basic oxide," which may be given by an equation of the form,

$$(O^{--}) = \Sigma(n_{MO}) = n_{CaO} + n_{MgO} + n_{MnO} + n_{FeO} - 2n_{SiO_2} - 3n_{P_2O_5} - n_{Al_2O_3} - n_{Fe_2O_3}$$

as discussed by the writer.[28]

It is probable that more oxygen ions are available from the breakdown of silicate tetrahedra.

$$SiO_4^{4-} \rightleftharpoons SiO_3^{--} + O^{--} \quad . \quad . \quad . \quad . \quad (4)$$

or

$$P_2O_5 + 3SiO_4^{4-} \rightleftharpoons 2PO_4^{---} + 3SiO_3^{--} \quad . \quad . \quad . \quad (5)$$

In other words, oxygen ions from sites on the silicate tetrahedra are also available for phosphate formation. The extent of reaction (4) could be arrived at by the application of methods such as those of Winkler and Chipman [28] and Murray and White.[29]

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[25] Losana, *Atti delle Raele Accad. Sci. Torino*, 1942–43, **78**, 194.

[26] Winkler and Chipman, *Trans. Amer. Inst. Min. Met. Eng.*, Tech. Publ., 1987.

[27] Balajiva, Quarrell and Vajragupta, *J. Iron Steel Inst.*, 1946, **153**, 115.

[28] Carter, This Discussion.

Whether other metallic ions can be included in the (Ca^{++}) term depends on the stability of the relevant phosphate. It is probable that (Mg^{++}) can be included, but not (Mn^{++}) or (Fe^{++}). Further knowledge of the stability of these phosphates in the presence of iron is required.

The writer finds it difficult to appreciate the explanation given by Bockris, Kitchener, Ignatowicz and Tomlinson, for the greater conductivity of $MnO–SiO_2$ compared with $CaO–SiO_2$ given in Table II of their paper, unless it is to be inferred that the breaking-up of the silicate structure due to the greater coulombic attraction of Mn^{++} for O^{--} can take place without the disturbed oxygen ions affecting the progress of the manganese ions during cationic conduction. In the same paper, this is also referred to as a disturbance of the structure of the silicate by the metal ions, which seems to describe the process better. The viscosity of the $MnO–SiO_2$ slag referred to in Table II is given by Towers and Gworek [30] as approximately 6 poises.

With regard to terminology, it is suggested that, to avoid confusion with past phraseology, where the word dissociation was used to describe reactions such as

$$2CaO . SiO_2 \rightleftharpoons CaO . SiO_2 + CaO \quad . \quad . \quad . \quad (6)$$

the word dissociation should not be used for the breakdown of a compound into ions, but that the term ionisation is more appropriate. One would therefore speak of the ionisation of FeO, rather than the dissociation of FeO. It may, however, be correct to speak of the dissociation of ions into simpler ions, as (6) is equivalent to

$$SiO_4^{4-} \rightleftharpoons SiO_3^{--} + O^{--} \quad . \quad . \quad . \quad . \quad (7)$$

Dr. T. P. Hoar (*Cambridge*) said : The importance of this pioneer work* makes one wish it had been possible to publish it with full experimental details The experimental results given in Fig 5–7 show many interesting anomalies—such as the large slope of curve 3 of Fig. 5, and the breaks in curves 4 and 6—that deserve the much more detailed recording that would warrant a fuller discussion. At present it is difficult to assess the accuracy of the derived results given in Table II and Fig. 2–4, on which the authors found a good deal of their discussion ; in particular, the important high values of E_κ and A for the 45 %–CaO composition in the $CaO–SiO_2$ system are not derivable from the experimental $\log \kappa - 1/T$ curve of Fig. 5, and the experimental curve from which are derived the corresponding values for the 65 %–MnO composition in the $MnO–SiO_2$ system is not given in Fig. 6.

With the general picture of cation migration through a relatively immobile magma of polysilicate anions, I am in agreement. The facts that the divalent cations appear in general to migrate more easily than the monovalent, while the tervalent Al^{+++} has very small mobility, appear explicable on the basis of size and charge ; the higher the charge, the smaller the ion and therefore the more easily can it pass through the polysilicate interstices, unless the charge becomes so high (3 +) that the ion remains more or less fixed to an $—O^-$ on the anion.

I do not agree with the authors' suggestion that a small cation such as Al^{+++} " has the effect of attracting some of the oxygen ions held in the silicate tetrahedra and thus breaking down the structure." The polysilicate structure must be broken down by the *addition* of oxygen ions—i.e., by the addition of any metallic oxide—as pointed out by Herasymenko in this Discussion.

Mr. R. P. Bradshaw and I are engaged in a study of conductivities of systems similar to those investigated by the authors, using a rather different experimental technique ; first results are imminent, and we look forward to the continuance of fruitful discussions and arguments with Dr. Bockris and his collaborators

Dr. J. O'M. Bockris (*London*) (*communicated*) : In reply to Dr. Carter, it seems necessary to stress that the ionic or molecular method of representing slag constitutions are neither nominally nor formally but *essentially* different. Convincing evidence on former differences is given in Willis's paper.

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[29] Murray and White, This Discussion.
[30] Towers and Gworek, *J. West Scot. Iron Steel Inst.*, 1943–44, 51, 123.

* Bockris, Kitchener, Ignatowicz and Tomlinson, This Discussion.

Dr. Hoar's criticism of lack of clarity in the presentation of graphs is admittedly justified. The length of the paper was already greater than that requested for the meeting. The value of E_κ for 45 % CaO – SiO_2 melt is, as he points out, too high. It is intended to publish further results in much greater detail.

I do not at present think, as Dr. Hoar does, that the size and charge of the ion are sufficient to explain the variation of conductivity of different systems with the same molar fraction of SiO_2 at the same temperature. Dr. Hoar perhaps somewhat misunderstands the model we suggest. We consider that the coulombic field of the cation tends at first to break up the silicate lattice and that this results in an increasing conduction (other conditions being the same) for increasing ion-oxygen attraction until the latter is sufficiently high for it to compete with that of Si^{4+}. When this is so (e.g., for Al^{3+}) there is a resultant lattice-forming effect (and not a breaking-down effect as Dr. Hoar assumes). This, we suggest, is why the conductivity increases with the ion-oxygen attraction for larger ions but decreases for Al^{3+}. This tentative theory can only be proved or disproved when values are available for a considerably greater number of ions than at present. In this connection we eagerly await news of Dr. Hoar's first measurements.

Dr. J. White (*Sheffield*) (*partly communicated*) : Dr. W. F. Ford and I have been carrying out a somewhat similar investigation[31] to that described by Dr. Bockris and his colleagues, and we have had several discussions with them. We have been concerned, however, mainly with the effects of melting on the electrical properties of our mixtures, which have been previously melted $CaO–Al_2O_3–SiO_2$ compositions, and the temperature ranges covered above the liquidus temperatures have been rather narrow so far. With this reservation we find that the log $\kappa–1/T$ plots of our mixtures are closely linear in the completely liquid state and in the solid state up to some 50°–100° c. below the (eutectic) melting point. We get activation energies of 20–30,000 cal./mole for the solid state, and probably rather higher than this for the liquid. Unlike those of the authors our curves represent steady values obtained after holding the temperature constant for a sufficient time at suitable intervals during heating or cooling. It is then found that the rise of conductivity associated with melting consistently begins below the melting temperature. (The curves of Wejnarth, to whose work the authors refer, indicate similar behaviour when compared with the corresponding thermal equilibrium diagrams.) Since the energy of activation obtained from the slope of a linear log κ plot is in reality the sum of an energy of disorder (or vacant site formation) and an activation energy of mobility, such behaviour can be formally accounted for in terms of a progressive co-operative decrease in the former term as the melting point is approached, thus constituting " premelting." It is difficult to be certain that traces of impurity may not be responsible, however, though the phenomenon appears to be of fairly general occurrence with silicates.

Supercooling readily occurs, not only on cooling from above the melting point but also on cooling from within the premelting range. In the latter case the return to equilibrium simulates a first-order reaction the velocity of which exhibits an inverse exponential relation with temperature, i.e., it increases, probably to a maximum, as the annealing temperature is decreased suggesting that some form of nucleation mechanism is involved.

Over the range of frequencies used (316–10,000 c./sec.) the capacity-temperature curves show a qualitative similarity to the conductivity-temperature curves in that the capacity rises steeply below the melting point, then more slowly once the melting range has been entered. At constant frequency, curves of $1/\omega CR$ (the tangent of the loss angle) against temperature show pronounced absorption maxima at temperatures close to the eutectic melting point, the peak temperature increasing slightly with increasing frequency. At constant temperature but increasing frequency peaks in the $1/\omega CR$ curves are also observed within the frequency range used at temperatures from the premelting range upwards.

Our experimental conditions differ from those of the authors in that we have worked in an oxidising atmosphere throughout using bright platinum electrodes. With these we find that both resistance and capacity vary appreciably with the frequency as might be expected from the foregoing. It is not possible to account fully at present for the differences between the authors' observations and our own but, bearing in mind the order of the relaxation times indicated for the absorption mechanism and the other relationships observed, it seems possible that with platinum some form of ionic separation in the vicinity of the electrode surface gives rise to polarisation effects. Molybdenum may take part sufficiently in the cell reactions to prevent this.

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[31] *Brit. Ceram. Res. Association Report* (in press).

Prof. J. Chipman (*Cambridge, Mass.*) said : In view of what has been said regarding our limited knowledge of the constitution of liquid slags, perhaps a few words are in order in support of the methods of calculation used by Murray and White.

The fact that the thermodynamic properties of slags can be recorded in the form of simple equations such as those here employed cannot be taken as proof, or even as an indication, that the formulæ represent molecular entities in the slag. I doubt that anyone who uses such formulæ imagines that he has thereby solved the problem of the constitution of slag. The authors specifically disavow any such claim and regard their treatment as "purely formal." It is possible in fact to represent a given set of thermodynamic data equally well by alternative groups of formulæ and equations by the simple expedient of introducing activity coefficients ; and this is equally true whether the formulation be in terms of compounds or ions.

The plain fact is that the thermodynamics of slags has advanced more rapidly than our knowledge of slag structure (perhaps because it is more interesting) We do not have a satisfactory structural model upon which to base our computations and are forced to improvise such formulæ as those used by Dr. White. The usefulness of such a set of equations should be judged only by its ability to reproduce the thermodynamic data. The fact that the equations here presented are able to do just this without the aid of activity coefficients other than unity adds the desirable element of simplicity to their evident utility.

Prof. M. Rey (*Paris*) said : It was pointed out by Dr. Bockris in the Discussion that the thermodynamic approach could not reveal the structure of the system studied nor provide a working model. I quite agree with him. Thermodynamics is a system of energy relations which is independent of the nature of the forces acting within the system, but I would like, however, to insist on the fact that the models of structure which are proposed must in all cases be in agreement with the thermodynamic relations. I shall point out two applications of this principle.

The first is, as Prof. Guggenheim remarked, that the variation in entropy during the melting of a silicate being small, the structure of the liquid silicate must be similar to that of the solid silicate. The second is related to the possibility of the presence of free metallic oxides in fused slags which has usually been assumed by metallurgists.

I have shown the great difference in thermodynamic behaviour between, say, the SiO_2–Na_2O system and the SiO_2–FeO system. The structures must, therefore, according to the above principle, differ appreciably. In the second the metallic cation tends apparently to retain its oxygen and this slows down the breaking-up of the silica structure. Dr. Richardson expressed the same idea when he said that the need for a high co-ordination of the metallic cation with oxygen was responsible for the behaviour of the system. The old conception of some free iron oxide in a fused iron silicate is, therefore, not without some basis. I would not agree with Dr. Guggenheim that this idea is so vague that it is without practical use. It has, in fact, been used by metallurgists with some success. But the point where the metallurgists have gone astray is in the estimate of this free iron oxide. They have assumed that a quantitative estimate was given by the ratio between the amounts of free oxide and total oxide. This estimate has validity only in systems which are not far from ideality. The correct estimate of the free oxide is not a measure of quantity of free oxide, but one of the degree of freedom of the oxide. In other words, it is a measure of the chemical potential or of the thermodynamic activity of the oxide.

Speaking in terms of chemical potential, I would say that in liquid iron or in fused calcium fluoride, which have a low *capacity* for dissolving iron oxide, or where the activity coefficient of iron oxide is high, the activity and chemical potential of iron oxide increase very rapidly with even small additions in contrast with slag systems which have a much greater capacity for dissolving the oxide. To my way of thinking, it is only in this sense that the old idea of Schenck and other metallurgists of the presence of free oxides in slags can be reconciled with facts and can be made really useful.

I would also like to comment on the activity of silica as shown in Fig. 5 of the paper by Murray and White. In their diagram, liquid supercooled silica is used as reference state. Now if eqn. (1) of my paper, or (1) of their paper (which is my equation reversed), is used to calculate the ratio between solid and liquid activity at 1600° C., using the value at 1835 cal. for the heat of fusion of silica derived by Kracek[32] (a value which I have used throughout) it is seen that the liquid activity is only 3 % less than the solid activity.

The solid activity is unity at the saturation point. Therefore the activity curve of silica must be much steeper than shown in the Figure between 40 and 65 molar % silica and must run very near to the horizontal between 65 and 100 molar %. It may be argued that my deductions depend upon the accepted heat of fusion of silica which is uncertain. The authors accept an old figure of 6800 cal./mole. But this figure is very likely erroneous and it is worth noting that Kelley,[33] in his review of the data available, adopts 2100 cal./mole as the best value.

However another argument can be given. If Fig. 5 was established, not for 1600° C. but for the melting point of cristobalite, it would, using the method of calculation of the paper, give an activity curve of silica only a little higher than the one drawn. In this case, liquid and solid activities would be identical and the activity curve of silica should, because of the gap in miscibility, be very close to unity at 72 molar % silica.

I believe that, because of the gap in miscibility on the silica side of the diagram, we must admit the presence of a bulge in the curve for the activity of silica, which cannot be accounted for by the assumption of an ideal solution of various constituents.

Finally, it should be noted that the agreement shown in the Figure between the curve drawn and the potentiometric determinations of Chang and Derge has no significance as the activities, in terms of cristobalite, given by these authors, have been arbitrarily multiplied by 0·509, the value assumed to represent the ratio between liquid and solid activities. The values of Chang and Derge are in agreement, as I showed, with the curve of activity of solid silica but they cannot be used as a check of an activity curve of the liquid.

Dr. J. O'M. Bockris (*London*) said: The inflections which occur in the log κ-$1/T$ relations for 35 % and 45 % CaO in the CaO–SiO_2 system are similar to those observed by Bloom and Heymann[34] for simple binary salts and by Martin and Derge[35] in the system CaO–Al_2O_3–SiO_2. A "premelting" phenomenon seems to be involved in most of these cases: in the system containing 45 % CaO in the present work, inflection appears approximately at the m.p., the more marked fall at the "solidification point" occurring at temperatures much below the m.p. as in most systems examined in our work. A closer investigation of the whole (rather complicated) behaviour of the conductivity in the region of the m.p. is planned.

Prof. Chipman maintains that by selecting the right compounds, the activity coefficients in slag equilibria can be reduced to the order of 1 and seems to imply that this supports the existence of such entities in liquid slags. As indicated above, this reasoning can never be good evidence for such structures whilst the thermodynamic equations can be thus satisfied in several ways.

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[32] Kracek, *J. Amer. Chem. Soc.*, 1930, **52**, 1436.
[33] *U.S. Bur. Mines Bull.*, No. 393.
[34] Bloom and Heymann, *Proc. Roy. Soc. A*, 1947, **188**, 392.
[35] Martin and Derge, *Trans. Amer. Inst. Min. Met. Eng.*, Tech. Publ., 1569.

Mr. D. W. Hopkins (*Swansea*) (*communicated*): The effect of the addition of oxides capable of combining with ferric oxide on the activity coefficient of the latter has been well brought out by Mr. Murray and Dr. White in their paper. The writer puts forward the following illustration of a similar effect which he has found in the zinc oxide-ferric oxide system on account of the correlation between the formation of the compound $ZnO . Fe_2O_3$ and the activity curve. Such correlation is only possible at temperatures where the compound is stable relative to the ferric oxide and so would not be apparent in the $CaO–Fe_2O_3$ example given. $ZnO . Fe_2O_3$ contains 33·76 % zinc oxide and is capable of dissolving ferric oxide at 1400° c.

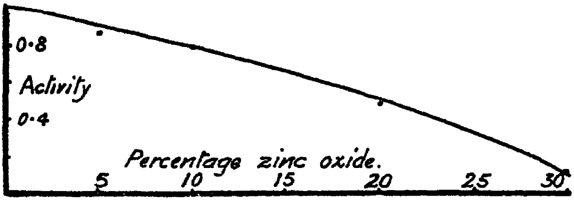

FIG. 1.—Effect of zinc oxide on the activity of ferric oxide at 1400° c.

Prof. B. Kalling (*Domnarvet, Sweden*) said: There is one thing of great importance that Mr. Fornander has clearly verified in his interesting paper. His investigations show that there is no connection between the content of manganese and that of oxygen in the steel bath during the boil in the steel furnace. That may not be surprising for those familiar with the modern physical chemistry of steelmaking, but the practical steel man, who, since ancient times, has had the experience that manganese in the charge is a necessary remedy to get a clean steel, has naturally explained this good influence as due to some deoxidation power of manganese in the furnace during the boiling period. Now we know that this is not the case, and we have to look for another explanation for this, surely over-valued, quality of manganese in the steel bath—a question of more technical character that I will not take the time to enter upon here.

There is another question in Mr. Fornander's paper: he has found that the actual oxygen content in the steel bath is much higher than the content in equilibrium with the carbon content thus indicating a sluggishness in the carbon reaction, probably due to the factors influencing the formation of the CO bubbles at the interface between the steel bath and the furnace bottom. This retardation of the carbon reaction will surely, in most cases, greatly influence the rate of the carbon drop, but I think it is misleading to give it too much responsibility for the slow boiling rate in the open-hearth furnace in general. The viscosity of the slag sometimes seems to be the dominating factor. The diagram in Fig. 1 illustrates the variation in FeO activity from the surface of the bath to the furnace bottom under conditions that are quite common during the boil in a basic open-hearth furnace according to Mr. Fornander's results. This diagram shows that the difference between the FeO activity in the slag and that in the steel bath is much higher than the difference between the latter and the equilibrium value. This must indicate that the transport of oxygen to the steel bath is retarded to a great extent by lack of convection in the slag and, maybe also, in the steel bath. As the convection is highly influenced by the viscosity of the slag, this factor must be considered as very important for the transport of oxygen to the steel and thus for the rate of the carbon reaction.

It may also be pointed out that the values of the over-saturation of oxygen in the steel which Mr. Fornander has mentioned and which agree very well with those found by Brower and Larsen do not seem to be in the same good agreement with some other results obtained in Sweden in the study of the acid open-hearth process as practised in our country. Table I shows some analytical results from a few heats taken from one of the papers to which Mr. Fornander has referred.* The figures have been chosen from three heats with very different slag compositions. It is, of course, dangerous to draw any definite conclusions from these few figures, but it may be permissible as they are rather representative of the results generally found in these investigations. It is remarkable that in this case the oxygen content in the steel bath is so very low in all the heats. The excess of oxygen is about zero. It seems as if the rate of carbon drop has not been greatly retarded by the physical conditions influencing the formation of the CO bubbles. There can, of course, be some uncertainty in the analysed oxygen values. The real oxygen content may be somewhat higher, but there is reason for the assumption that the eventual difference is very small in this case. I think that the very low content of excess oxygen in the acid open-hearth heats can be explained in the following way.

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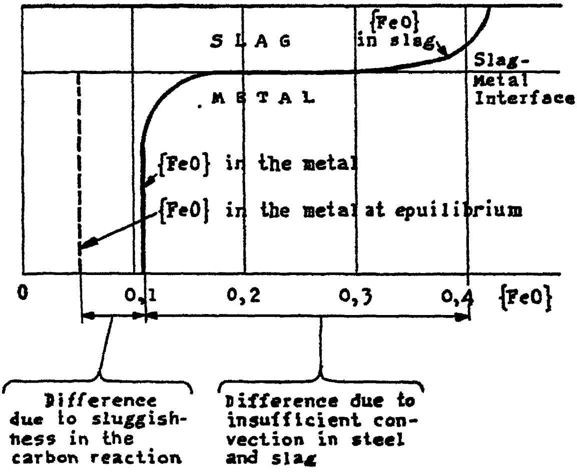
* Ref. 19 in Fornander's paper.


S L A G
{FeO} in slag
Slag-Metal Interface
METAL
{FeO} in the metal
{FeO} in the metal at epuilibrium
0
0,1
0,2
0,3
0,4
{FeO}
Difference due to sluggishness in the carbon reaction
Difference due to insufficient convection in steel and slag

ASSUMPTIONS—
Temperature: 1600° c.
{FeO} in Basic Slag with 25 % FeO . . . . = 0.40 %
Oxygen Content of Pure Iron in Equilibrium with Pure Iron Oxide at 1600° c. = 0.22 %
Oxygen Content of Steel with 0.25 %*C at* 1600° c. (*and Equilibrium*) . . = 0.010%
Oxygen Content of Steel with 0.25 %*C at* 1600° c. (*actual*) . . . . = 0.025%
{FeO} in Steel with 0.25% *C* at 1600° c. (*Equilibrium*) . . . . = 0.045%
{FeO} in Steel with 0.25 %*C* at 1600° c. (*actual*) . . . . . = 0.115%

FIG. 1.—Schematic diagram showing FeO-activity during the boiling period in the steel furnace.

An essential feature in the acid open-hearth steel-making in Sweden is the very pronounced reduction of silicon in the steel bath at the end of the boiling period. It is obvious that this silicon is reduced from the acid furnace bottom and not from the slag. The slag has, on the contrary, an oxidising influence on the silicon in the steel. There is in this way a stream of silicon passing from the bottom to the slag. This reduction of silicon from the bottom will probably cause a very clean and porous hearth that will highly facilitate the formation of CO bubbles and thus decrease the excess of oxygen in the steel. This may be a reason why it has been found easier to make a clean high-quality steel in the acid open-hearth furnace than in the basic one. Another factor that perhaps has to be taken into consideration is that the bottom surface area per ton steel is bigger in a small than in a big furnace. This will also result in a smaller value of the excess of oxygen.

The composition of the slag in the three different acid heats confirms in an obvious way Mr. Fornander's results that the FeO activity of the slag has not much influence on the oxygen content in the steel bath. The FeO content in the slag in the first heat when the samples were taken is about 27 %, but in the second heat with the high manganese slag only 7·6 %. In both cases the excess of oxygen is about zero and the rate of carbon drop about the same. That the transport of oxygen from the slag into the steel has not been greater in the first heat than in the second must be due to a much higher fluidity of the high manganese slag The variation in the FeO activity in the three acid heats is illustrated in Fig. 2.

It is interesting to note that when working with high manganese content in the slag in an acid open-hearth furnace it is possible to get about the same composition of slag and metal during the boiling as in a Bessemer converter using high manganese metal in spite of the much higher convection rate in the converter.

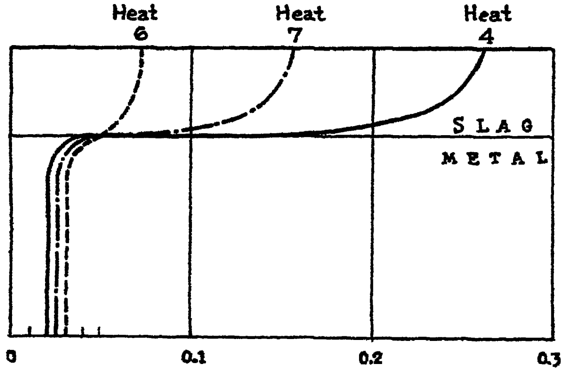


FIG. 2.—FeO-activity in the different acid open-hearth heats.

TABLE I

COMPARISON OF STEEL AND SLAG COMPOSITIONS DURING THE BOIL IN SOME ACID OPEN-HEARTH HEATS

Heat No.		4	6	7
Steel: C %		0·55	0·45	0·64
Si %		0·138	0·230	0·136
Mn %		0·10	0·48	0·14
O %		0·0040	0·0065	0·0055
Slag: SiO_2 %		54·5	50·9	60·1
FeO %		26·9	7·6	13·8
Fe_2O_3 %	about	0·9	0·0	0·3
MnO %		15·5	35·61	15·7
Al_2O_3 %	about	1·1	1·36	1·57
CaO %	about	0·5	1·80	7·20
MgO %	about	1·1	2·69	1·52
Rate of Carbon Drop:				
$\frac{dC}{dt}$ % C/hr.		0·28	0·31	0·48
C % × O %		0·0022	0·0029	0·0035
" Excess oxygen " %	about	Nil	0·001	0·0015
{FeO} in slag	about	0·25	0·07	0·13
{FeO} in steel (actual)	about	0·020	0·030	0·025
{FeO} in steel (equilibrium)	about	0·020	0·025	0·020

Mr. H. Willners (*Trollhaettan, Sweden*) said: I am very impressed by Mr. Fornander's interesting paper and I think that the experimental data published by him are a most useful contribution to the clarification of the problems he has discussed. There is just one point on which I do not quite agree with him.

In his summary he declares rather definitely that the manganese content of the charge has no influence on the oxygen content of the bath and on the rate of carbon drop, but his Fig. 14 does not seem entirely to bear out his statement. A rough calculation on the basis of his plots gives the result that the average rate of carbon drop, expressed in 0·01 % C per 10 min., is about 7·7 for 0–0·8 % Mn in the charge, but about 8·9 for the heats with more than 1·4 % Mn in the charge. This is an increase of about 15–16 % in reaction speed and if any conclusions are to be drawn from these plots it should rather be that Mn seems to have a tendency to increase the rate of carbon drop, although the oxygen content in steel is the same as usual. (See his Fig. 12.)

If the formation of CO bubbles in the bath is the "bottle-neck" of the reaction, the velocity of carbon drop is a function of

(1) the so-called carbon and oxygen pressures in the steel, which are determined by the carbon, viz., oxygen content, and what I should prefer to call the specific activity of these elements, i.e., the activity per unit carbon and oxygen;

(2) the temperature; and

(3) the probability of forming nuclei for the gas bubbles.

Provided that the experimental results are sufficient to allow an interpretation Fig. 12 and 14 show that an increased Mn content in the charge has a tendency to increase the velocity in spite of the oxygen and carbon content in the steel being the same as usual. That Mn would increase the carbon activity is not very likely. From what we know of the influence of Mn on pig-iron and cast-iron, and the effect on graphitisation, it is more likely that Mn will decrease the specific activity of carbon instead of increasing it. The influence of temperature is, as Mr. Fornander states, still uncertain, as too few accurate measurements have been made. The influence of Mn on the probability to form nuclei is still more uncertain; about that we know practically nothing and every assumption is hardly more than a guess. There remains, however, the possibility that Mn increases the specific activity of oxygen in iron.

This is not contradicted by the fact that the rate of carbon drop can be still more influenced by other factors, for instance the rate of addition of ore to the bath, nor has it anything to do with the experience that, with still higher Mn contents in the steel, conditions are so changed that the boiling process will slow down, possibly due to what is sometimes called the deoxidising effect of Mn. It merely coincides with the well-known experience in the melting shops that *up to a certain point* Mn is liable to facilitate the oxidation of carbon.

Until the other factors mentioned above have been more thoroughly investigated we can say, from Mr. Fornander's result, that Mn influences the rate of carbon drop in the same way as if it increased the specific activity of oxygen in steel, and, it seems to me, we can continue to regard this theory as a reasonable working hypothesis.

Dr. F. D. Richardson (*B.I.S.R.A.*) (*communicated*): The results depicted in Fig. 13 of Mr. Fornander's paper are of interest in connection with his view that the rate of carbon removal is controlled by the rate of bubble formation on the furnace bottom. Bubbles will form most easily at crevices on the bottom, which already contain small quantities of gas, introduced either in the fettling process or left over from the previous melt. Any tiny gas pocket in such a crevice will grow as carbon monoxide is formed at its interface by reaction between the carbon and oxygen dissolved in the metal. Growth will continue until the pressure of carbon monoxide inside the pocket is in equilibrium with the concentration of carbon and oxygen outside. As the bubble grows, its radius of curvature must, of necessity, decrease until, for a crevice of circular cross-section, the bubble becomes hemispherical. Thereafter the radius will increase until the bubble finally detaches itself and floats up through the metal, leaving behind a residual pocket of gas from which a fresh bubble can form. Since the difference in pressure between the exterior and the interior of the bubble, due to surface tension, is a maximum at the minimum radius of curvature, it follows that any particular crevice can serve as a continuous source of bubbles provided the total pressure in the bubble, when it reaches the hemispherical condition, is less than the carbon monoxide pressure (p_{CO}) in equilibrium with the local carbon and oxygen contents of the metal. That is,

$$p_{CO} = K[C][O] = 1 \text{ atm.} + p_{Fe} + 2T/r,$$

where p_{Fe} is the ferrostatic pressure at the bottom, T is the surface tension of the metal and r is the radius of the crevice.

For any reasonable rate of elimination of carbon it is essential to have a reasonable number of suitable sites acting as bubble starters. For the same furnace conditions one would therefore expect the excess value of p_{CO} over and above one atmosphere to remain roughly constant throughout the refining period. If a line is drawn in Fig. 13 showing the [C] [O] product for an equilibrium pressure of *two* atmospheres at 1600° c., by doubling the values already plotted for *one* atmosphere, this can be seen to be approximately the case. The line passes through the mean of the points except at the end of the process, when the reaction is presumably slowing down and a smaller number of larger sites are acting as bubble starters. It is of interest to observe that for an iron depth of 16 in., a value of p_{CO} of 2 atm. as suggested by Fig. 13, and a value of 1500 dyne/cm. for the surface tension of the liquid iron, r is equal to 4×10^{-3} cm. For a crevice which is not circular, but is a narrow channel, T/r should be substituted for $2T/r$ in the equation, as the curvature in one direction will be negligible compared with that in the other. The shorter dimension of the smallest channel crevices functioning in this way would therefore be twice the radius of the circular crevice.

Mr. Malcor (*Paris*) said : I am very much interested in Mr. Fornander's very useful paper. As one of the few steelmakers present at the meeting I would like to point out, however, that it is very difficult to draw from experiments in steel plants sure conclusions about equilibria. The correlations found between two elements by studying the course of a melt are controlled not only by equilibrium laws but also by relations of a simple stoichiometric nature.

Let us, for instance, consider a bath of molten steel below a slag composed only of FeO and MnO. If both the equilibria of C and Mn were reached we might write :

$$[C] \times (FeO) = K_1\text{; at } 1600° \text{ c., } K_1 = \begin{cases} 0{\cdot}60 \times 10^{-4} \text{ for C} = 0{\cdot}2\ \% \\ 0{\cdot}91 \times 10^{-4} \text{ for C} = 0{\cdot}7 \end{cases}$$

$$[Mn] \times \frac{(FeO)}{(MnO)} = K_2\text{; at } 1600° \text{ c., } K_2 = 0{\cdot}4 \times 10^{-2}.$$

But we have also :

$$(FeO) + (MnO) = 1$$

so that

$$\frac{[Mn]K_1/[C]}{1 - K_1/[C]} = K_2$$

or

$$\frac{[Mn]K_1}{[C] - K_1} = K_2$$

Since K_1 is very small compared to [C] (less than 0·01 %), we have

$$\frac{[Mn]}{[C]} = \frac{K_2}{K_1} = \frac{0{\cdot}4}{0{\cdot}007} = 60.$$

By the same method, we obtain the relation :

$$[Mn] \times [FeO] = K_2\,(L_{FeO} - [FeO])$$

or, as $L_{FeO} > [FeO]$,

then $$[Mn] \times [FeO] = K_2 L_{FeO}.$$

This means that if both equilibria were reached the manganese content in steel would be proportional to the carbon content and inversely proportional to the oxygen content.

With the acid open-hearth practice used on the Continent, conditions are substantially the same but

$$FeO + MnO = 0{\cdot}4$$

and $$K_2 = 0{\cdot}085\ \%.$$

Therefore $$\frac{[Mn]K_1}{0{\cdot}4\,[C] - K_1} = K_2$$

or $$\frac{[Mn]}{[C] - 2{\cdot}5K_1} = \frac{0{\cdot}4K_2}{K_1} = \frac{0{\cdot}4 \times 0{\cdot}085}{0{\cdot}007} = 5$$

or $$\frac{[Mn]}{[C]} - 5.$$

In this case it is well known that the carbon-oxygen equilibrium is not reached; therefore the proportionality of carbon content to manganese content is not observed.

Some months ago, Achard pointed out that in basic electric-arc furnaces the carbon and manganese contents of the steel were correlated to a certain extent as shown in Fig. 1. Before an apparent equilibrium is reached, manganese decreases alone; then both carbon and manganese decrease, the quantity $\frac{[Mn]}{[C]}$ being roughly constant. Up to now, no satisfactory explanation of this phenomenon has been found. My only conclusion will therefore be that one has to be very cautious about the interpretation of theoretical equilibrium laws and it would not be safe to assume that there is never a connection between manganese and oxygen content of the steel.

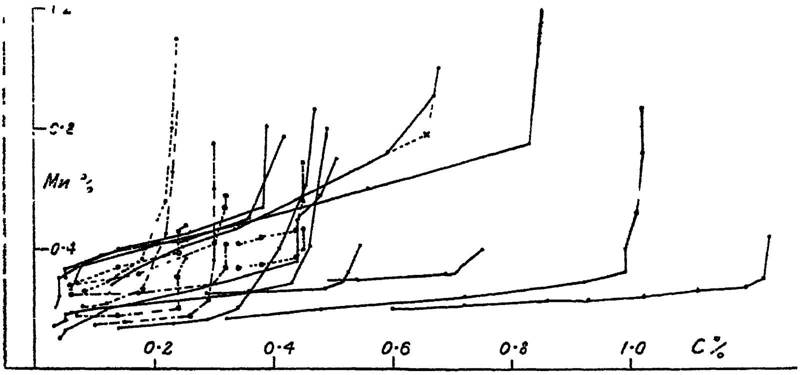


FIG. 1.

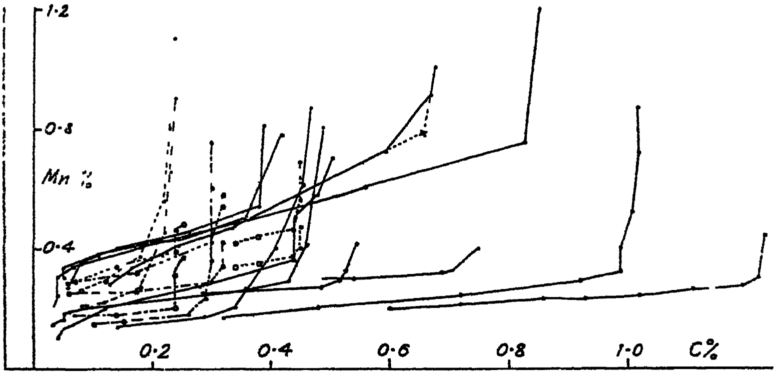


FIG. 2.

Dr. P. Herasymenko (*Sheffield*) (*communicated*): The work of Mr. Fornander is an important contribution to our knowledge on the carbon-oxygen reaction in liquid steel. Although this reaction forms the basis of steelmaking, the published information on the composition of steel and slag during the refining period in the open-hearth furnace was relatively scarce. With respect to the data of slag composition it would be desirable to know the content of ferrous and ferric iron in slag instead of the total iron content (expressed as FeO) as reported by Mr. Fornander.

The work of Mr. Fornander verifies the important discovery made by Körber and Oelsen[36] that the carbon-oxygen reactions is essentially a heterogeneous

[36] Körber and Oelsen, *Mitt. Kaiser-Wilhelm Inst Eisenforsch* 1935, 17, 109.

reaction. At the same time Mr. Fornander's data disprove some exaggerated conclusions made by the workers of the Kaiser-Wilhelm Institute.

Körber and Oelsen have found that the rate of carbon elimination in the homogeneous liquid iron is very low and is greatly accelerated by the crystalline surfaces such as of solid silica or solid iron crystals. In presenting their results, Körber and Oelsen accepted a purely physical explanation of the phenomenon. They assumed that the primary reaction between carbon and oxygen proceeded very fast in the homogeneous liquid steel and the carbon monoxide formed remained in supersaturated form. The crystalline substances acted as catalysts in the formation of the bubbles of CO. Once the gas-metal interface was formed it took over the largest part in the further catalysed evolution of carbon monoxide. Körber and Oelsen laid too much stress on this catalytic effect of gas-metal interface, the crystalline substances being described only as the initiators of the gas bubbles. This led them to the conclusion that the oxygen content of the boiling bath should decrease very soon to a value which corresponds to the equilibrium between carbon and oxygen. Mr. Fornander accepts the views of Körber and Oelsen, although his own data as well as earlier results of Brower and Larsen do not conform with this theory. If the rate-determining process were the formation of bubbles, then the oxygen content—which is low at the beginning of the boil—should follow the curve of equilibrium with carbon, or, in other words, the supersaturation should disappear. Fig. 12 of Mr. Fornander's work does not show such tendency. In terms of Körber and Oelsen's theory, Fig. 12 would indicate that the supersaturation does not decrease in spite of the greater opportunity to avoid supersaturation.

Further, the theory of Körber and Oelsen required that the rapid boil should lead to an increased reduction of manganese and phosphorus. The calculations of Larsen show that distribution of manganese and phosphorus between slag and metal is governed by the equilibria of these reactions and not by the rate of carbon elimination. Therefore, the purely physical theory seems to be untenable.

It seems to be more justified to accept that the slowest process which determines the overall rate of carbon elimination is the primary reaction between carbon and oxygen atoms. The process requires a high activation energy. The crystalline bodies lower this energy and act as catalysts. The cause of the high activation energy is unknown, and the actual state in which carbon and oxygen atoms exist in liquid steel needs further experimental investigation. Due to comparative slowness of the carbon-oxygen reaction, which proceeds mainly on the hearth bottom, oxygen in metal reaches its equilibrium value with the slag with the same ease as other elements, manganese, phosphorus, sulphur, etc. The contents of oxygen in the bath in equilibrium with the slag are lower in the presence of carbon than in "carbonless" steel, because carbon modifies the physicochemical behaviour of the metal phase and increases the activity of oxygen.

From the investigation of equilibria in the acid open-hearth furnace the following values for the activity coefficient of oxygen at various contents of carbon can be derived if the activity coefficient of oxygen in "carbonless" steel is put equal to unity (Table I).

TABLE I

[C] %	Activity coefficient of oxygen.
0·0	1·00
0·25	1·26
0·50	1·58
0·75	1·93
1·00	2·27

It has been found in a recent investigation [27] that these coefficients can be applied also to oxygen in basic steel. In this work we try to show, on the basis of the ionic theory of slag composition, that the equilibrium, $Fe_{metal} + O_{metal} = Fe^{++}_{slag} + O''_{slag}$, determines content of oxygen in steel. It was found that the equilibrium ratio of this reaction depends on the content of oxygen ions according to the formula,

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[27] Herasymenko and Speight (unpublished work).

$$k_{o}^{Fe} = \frac{(Fe^{++})(O'')}{[O]} = A(O'')^{3/2},$$

where A is a constant. By means of this formula oxygen contents in "carbonless" steel can be calculated from the content of Fe^{++} and O'' ions in slag. By assuming the validity of the above activity coefficient for oxygen, calculations of the content of oxygen in basic open-hearth steel at various contents of carbon are in substantial agreement with the observed values. To our satisfaction we find that the data of Mr. Fornander can be interpreted in the same way.

Mr. Fornander rightly concluded that attempts to calculate the rate of carbon reaction on the assumption that it is a homogeneous process are unfounded and could not be successful. The reaction is a typically heterogeneous one and may strongly depend on the condition of the hearth surface. We must not, however, dismiss entirely the possibility of being able to calculate the reaction rate. It is known that the rate of carbon elimination varies within comparatively narrow limits in the normal process of steelmaking in the open-hearth furnaces. Thus, it is probable that the catalytic effect of hearth surface can be accounted for numerically, if the effect of other physical factors (e.g., temperature) are known better and, of course, if the methods of oxygen determination are sufficiently exact.

Mr. F. L. Robertson (*Mold, Flints*) said: Coming as I do straight from the shop, I feel very shy about speaking to scientists. I wish, however, to ask Mr. Fornander, a brother steelmaker, a question and my embarrassment goes. Mr. Fornander has come out strongly on the side of those who regard residual manganese, during the working and at the end of a charge, to have no effect on the oxygen content of the steel. The oxygen content is governed by quite different factors. This is a view with which I thoroughly agree and which I think follows from the manganese-iron oxide equilibria studies of the last twenty-five years or so. There remains, however, the age-long belief among melters that a high residual manganese is most beneficial. Prof. Kalling has just shown a slide giving, for acid practice, residual manganese, varying from 0·1 % to 0·45 % Mn. To-day, basic steel worked down to 0·06 % carbon is made with 0·1 % to 0·3 % residual manganese. Which is the better steel ? When I started melting some forty years ago, we all said the high residual manganese was. Now is this a prejudice of ignorant and perhaps pig-headed melters or does it rest on a chemical principle ? The effect of the residual manganese on the oxygen content of the steel has been cut from under our feet by other workers and now again by Mr. Fornander. So if there is virtue in residual manganese, wherein does it lie ?

In this section, on slags and refining processes, it may not be out of place to note the absence of favourable reference to Schenck's text-book. Schenck's book is the only text-book that handles steelmaking by the application of the partition law, the law of mass action, and dissociation. He has marshalled a mass of observations into a system that lets us do badly-wanted sums on the melting stage. The sums work both in acid and basic melting and, to the great assistance of the melter, have a surprisingly wide application. That Schenck's system of marshalling thousands of observations in steel making, may prove insufficient and may neglect newer scientific principles that have been discussed at this meeting, may be true. All the same may I beg that the Faraday Society does not rob us of the first and, still, only shop-applicable text-book on the physical chemistry of steelmaking, without giving to steelmakers another.

Dr. A. H. Leckie (*B.I.S.R.A., London*) said: Dr. Carter in his paper has summarised the existing data on sulphur and has arrived at a very simple equation which may be rearranged as

$$[S] = k\frac{[O](S)}{\Sigma({}^{n}MO)}.$$

It is very important to establish the fundamental validity of this expression as it accounts for so many of the phenomena that are observed in practice.

The problem is to reduce [S] to a low value. The above relationship shows that this may be done by reducing [O] and (S) and increasing the activity of the bases

MO. In the normal electric furnace process desulphurisation is not a problem because in this process, by means of the so-called reducing slag, it is possible to attain a very low value of [O]. This is not possible in the open-hearth process, where the atmosphere has always a relatively high oxygen potential. Whilst the finding of Grant and Chipman, that the range of [O] found in basic open-hearth operation does not affect [S], is in apparent conflict with Carter's simple relationship above, and also with the views of some other investigators, this is not a serious matter affecting the practical application. As Mr. Fornander has proved, [O] depends on [C] so that [O] does not represent a degree of freedom but is largely governed by the specification of the steel being made.

Since in the open-hearth process one has little freedom as regards [O], the elimination of sulphur has to depend on the other parameters. In practice, the steelmaker relies on the increase of slag basicity $\Sigma({}^{n}\text{MO})$ and whilst this operation is effective, it is expensive and somewhat inefficient. Appreciable quantities of lime have to be added to the slag-forming materials and not only does this require additional time and energy for heating and fusion, but the lime addition is not 100 % efficient for its purpose. The lime tends to desulphurise the furnace atmosphere as well as the metal. The making of low sulphur steel by increasing slag basicity is therefore a costly process. There remains the possibility of decreasing (S), without decreasing (S)/[S].

Apart from the possibility of diluting the slag by increasing its bulk, which is open to obvious practical objections, this means the passage of sulphur from the liquid to the gaseous phase within the furnace. Whilst numerous investigators have studied equilibria between slag and metal, and between gas and metal, information on slag-gas relationships is scanty and further work on slag-gas systems would be of interest. If it is possible to secure substantial movement of sulphur into the gas phase, the low sulphur steel ([S] below 0·03 %) demanded for deep pressing purposes could be produced with much decreased slag bulk and at lower cost. The importance of the slag-gas equilibrium is emphasised by the fact that if a sulphur balance is prepared, one finds that roughly three-quarters of the mass movement of sulphur in the open-hearth furnace system occurs in the gas phase.

This example is an illustration of the argument put forward early in Dannatt and Ellingham's paper, that the physical chemist should have sufficient knowledge of plant requirements and conditions so that his answer may be readily translated into practice. It is to be hoped, therefore, that increasing attention will be paid to elucidating the conditions under which sulphur can be made to pass from the liquid slag to the gas phase within the furnace.

Regarding Mr. Fornander's paper, the only item which the writer would wish to question is the choice of symbols used. The symbols [X] and (X) for the concentration of the elements X in metal and slag respectively have been used by steelmaking chemists for some years and may be regarded as accepted. The increasing interest being shown in concentrations in the gas phase has resulted in the symbol {X} for concentration in the gas phase being used in this country, though this symbol has not, perhaps, reached the stage of general acceptance. Mr. Fornander uses this symbol for activity in the metal phase, and uses |X| for concentration in the gas phase.

In view of the desirability of standardisation of symbols, which was particularly stressed by Sir Andrew McCance in his opening remarks, some agreement on these symbols should be reached as soon as possible.

The writer suggests that the shape of the brackets should be restricted to a description of the phase in which the element occurs, and that the notation a_X should be used to denote the activity of X, which should be enclosed in brackets appropriate to the phase being considered. The symbol a is generally used throughout the papers, and the notation used by Mr. Fornander, if extensively adopted, is liable to result in complication and confusion particularly if activity in all three phases comes to be considered.

Dr. F. D. Richardson (*B.I.S.R.A.*) (*partly communicated*) : Dr. Carter's Fig. 3 and his eqn. (9) sum up our present knowledge of the partition of sulphur between iron and basic slags. Since there appear to be many different views concerning the factors controlling this partition, it is of interest to consider the physical significance of this finding, which is, in fact, quite independent of the manner in which these liquid slags may be ionised.

In this discussion I propose to consider only simple silicate slags in which the ratio of metal oxide to silica is in excess of that required to convert the whole silica network to separate SiO_4 tetrahedra, as indicated for fayalite in Fig. 2 of my own paper. In such slags, therefore, it will be possible to distinguish between two types of oxygen atoms, i.e., those attached to silicon and hence part of the SiO_4^{4-} ion, and those which are associated only with the metal atoms Ca, Mg, Fe, etc., and may reasonably be considered as O^{2-} ions. Dr. Carter's eqn. (9) leads to the equilibrium equation,

$$[O] + (S_{slag}) = [S] + (O_{slag}),$$

where (O_{slag}) and (S_{slag}) are unattached to silicon. It follows that sulphur from the metal can only enter the slag by displacing oxygen atoms unattached to silicon and that the energetics of this displacement are independent of the relative proportions of the different metal oxides. It is of interest to see whether this now checks reasonably with our present knowledge of the thermodynamics of the oxides and sulphides of these metals. If, as suggested by Kheinemann,[38] the data in Dr. Carter's Fig. 3 are replotted as $(S_{slag})/(O_{slag})$ against [S]/[O], the slope gives an equilibrium constant for the above equation, which with other appropriate data, leads to a value of —24·5 kcal. for $\Delta G°$ at 1600° C. for the change,

$$\tfrac{1}{2}O_2 + (S_{slag}) = \tfrac{1}{2}S_2 + (O_{slag}).$$

This may be compared with the values derived from thermal data for the following reactions involving the conversion of pure sulphides to pure oxides at this temperature,

$$\tfrac{1}{2}O_2 + CaS \rightarrow \tfrac{1}{2}S_2 + CaO \quad -21{\cdot}7 \text{ kcal.}$$

$$\tfrac{1}{2}O_2 + Fes \rightarrow \tfrac{1}{2}S_2 + FeO \quad -20{\cdot}8 \text{ kcal.}$$

$$\tfrac{1}{2}O_2 + MnS \rightarrow \tfrac{1}{2}S_2 + MnO \quad -26{\cdot}6 \text{ kcal.}$$

The similarity between all these values gives full support to the mechanism proposed and also indicates that the excess oxygen atoms in these slags act with respect to sulphur in the same way as the oxygen atoms in the pure oxides. Substitution of sulphur for oxygen atoms attached to silicon is doubtless possible, but must be energetically unfavourable compared with the other process.

It has been suggested by Grant and Chipman that two different mechanisms may be necessary to explain the marked effect of the FeO content of slags on the high values of (S %)/[S %], obtained under conditions where the metal contains very little oxygen, and the relatively small effect of FeO under the more oxidising conditions corresponding to the open hearth. The reason for this difference lies, of course, in the fact that addition of FeO to a basic slag of a fixed lime/silica ratio has two effects. It causes an increase in the number of oxygen atoms replaceable by sulphur, at the same time as it increases the FeO activity, and hence the value of [O %] in the equilibrium equation. At low FeO concentrations, additions of FeO can bring about little change in the number of replaceable oxygen atoms, but can cause relatively large increases in the values of [O %]. At higher FeO concentrations, the two effects tend to offset one another and the net effect is small. It is of some interest also to consider the manner in which the sulphur equilibrium is controlled in acid slags, in which there is no stoichiometric excess of oxygen atoms over those required to be attached to silicon. The sulphur may substitute for oxygen attached to silicon, entering itself into the silicon tetrahedra, or it may substitute for oxygen without entering the tetrahedra provided a silicate chain is lengthened at the same time, as represented by the equation,

$$2(SiO_4)^{4-}_{slag} + [S] = (Si_2O_7)^{6-}_{slag} + [O] + (S^{=})_{slag}.$$

Alternatively it may enter the holes between the silicon tetrahedra associated with an iron cation in a way similar to that in which sulphur occurs in ultramarine. The work of Holbrook and Joseph,[39] shows that even with acid slags oxygen is expelled as sulphur enters, the oxygen in their experiments being evolved as carbon monoxide after reacting with the carbon-saturated iron. Although not conclusive their results suggest that the last alternative is not important and that attention must be fixed on the first two. Complete equilibrium studies on acid slags require to be done before any definite decision can be made.

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[38] Kheinemann, *Bull. Acad. Sci. U.R.S.S.*, 1946 (No. 10), 1439.

[39] Holbrook and Joseph, *Trans. Amer. Inst. Min. Met. Eng.*, 1936, **120**, 104.

With regard to Dr. Leckie's suggestion concerning the passage of sulphur from the metal to the gas phase via the slag, I can say that on thermodynamic grounds the process is quite feasible, and might possibly be made of importance in the open-hearth furnace. At the slag-metal and slag-gas interfaces the equilibria can be represented by the equations,

$$[O] + (S_{slag}) = [S] + (O_{slag}),$$
$$\tfrac{1}{2}O_2 + (S_{slag}) = \tfrac{1}{2}S_2 + (O_{slag}).$$

The chemical potentials of oxygen and sulphur in the metal and in the gas phase are, in general, very different. For instance, even when saturated with oxygen, the potential in the metal corresponds to an oxygen pressure of about 10^{-8} atm. at 1600° c., whereas that in the gas corresponds to 10^{-5} atm. for producer gas 90 % combusted. If secondary complications resulting from this great change in oxygen potential are neglected for the moment, it will be recognised that provided the sulphur potentials in the metal and gas do not differ by a corresponding amount, a slag in equilibrium with the metal should give up sulphur to the gas. Detailed examination of the problem has shown that even when the body of the slag and metal are not in equilibrium with each other, transfer should occur provided the sulphur contents for metal, slag and gas are reasonable and the degree of combustion of the heating gases in contact with the slag is 70–80 %. It can also be said that complications, such as the oxidation of the iron oxides at the slag-gas interface, are likely to favour the process still further. Whether the transfer is significant depends on kinetic considerations, which we are now beginning to investigate. To achieve any transfer in practice it is obviously desirable to prevent partially combusted gas from striking the slag surface. This can be greatly assisted by good port design and the use of oxygen to give short flames in oil-fired furnaces.

Dr. P. T. Carter (*Glasgow*) (*communicated*) : The contributions to the Discussion by Dr. Leckie and Dr. Richardson are valuable in that they clarify further the theory underlying sulphur removal in steelmaking. Dr. Leckie has pointed out that Mr. Fornander's work indicates that [O] is not an independent variable. I agree substantially with this, although an analysis of Mr. Fornander's data suggests that towards the end of the refining period, i.e., at low [C], [O] is not entirely independent of (ΣFeO). It is unfortunate that it is not possible to show whether this is due to temperature variations, as temperature measurements are not given. The observations of Dr. Richardson give both an excellent picture and a more precise thermodynamic background, although the dual role of iron oxide in the slag was fully realised and has been pointed out before.

It is not without significance that, if certain groupings of atoms, e.g. M_2SiO_4, are assumed to exist in the liquid slags, (S_{Slag}) and (O_{Slag}) are equal to their respective activities (or at least bear the same proportional relationship to these activities) and that on this basis, basic slags can be regarded as behaving ideally when the sulphur equilibrium is being considered. It becomes more significant when it is realised that these compounds also exist in the solid slags, and suggests that the assumption of such groupings of atoms in the liquid state is not so " formal " as has been stated.

Dr. Leckie and Dr. Richardson justifiably discuss the importance of the gas-phase in sulphur removal. For conditions of complete combustion, sulphur will be removed from the slag for all normal sulphur concentrations irrespective of the basicity. On the other hand, under less complete combustion conditions, the high basicity which increases sulphur transfer from metal to slag also favours the passage of sulphur from gas to slag, as shown by the equation (using the nomenclature of Dr. Richardson),

$$O_{Slag} + \tfrac{1}{2}S_2 + CO \rightleftharpoons S_{Slag} + CO_2$$
$$(S_{Slag}) = K\,\frac{(O_{Slag})\,.\,p_{S_2}^{1/2}\,.\,p_{CO}}{p_{CO_2}}$$

An increase in basicity increases (O_{Slag}).

In cases where it is not possible to adjust combustion conditions to give low sulphur in the bath, more efficient sulphur removal by the formation of a second slag either inside or outside the furnace should not be overlooked.

Dr. M. Tigerschiöld (*Stockholm, Sweden*) said : Referring to the interesting experiments made by Wood I should like to mention some experiments that we made in Sweden. The coke or charcoal consumption in a blast furnace is very much dependent on the degree of oxidation of the ore used. We found that, for example, a dense magnetite will be much more easily reducible if it is roasted in oxidising atmosphere to almost pure Fe_2O_3 before being charged in the blast furnace.

We also found that it was very essential to control the sintering process so that a highly oxidised porous sinter was obtained. In the blast furnace the Fe_2O_3 is reduced very quickly at a relatively low temperature. The oxygen thus removed leaves pores in the ore which facilitate the further reduction of the Fe_3O_4 and FeO. The coke consumption is often 20 % or more when using a dense magnetite and the same ore in a roasted condition. In my opinion this fact is not recognised widely enough, and the sinter produced in America as well as in the great steel-producing countries in Europe very often is much too " hard-burned " and thus difficult to reduce.

Sir Charles Goodeve (*B.I.S.R.A., London*) said : In concluding the discussion, I will not attempt to summarise but will only give a few of my main impressions. The Faraday Society has, true to its traditional policy, gathered together scientists with a wide range of interests to discuss a specialised field. In addition to experimental and theoretical physical chemists, we have steel and other metal makers, metallurgists and theoretical physicists, all talking the same language !

The fact that a somewhat similar Discussion was held twenty-three years ago makes it convenient to assess what has happened in the interval. At that time, the application of the law of mass action was the main theme. This has substantially given way to free energies and chemical potentials. The volume and accuracy of the information available today is very much greater but there is need for further simplification in the treatment if this growing mass of data is to be usable by all the people who need it. The interval has seen the birth and growth of the science of reaction kinetics and diffusion, but there is still a great deal to be done before this complementary aspect is brought into balance with the thermodynamic viewpoint. In the background of this Discussion, one realises also that very big advances have taken place in our physical knowledge of the liquid and solid states. These advances are making possible a fuller development of the chemistry of the inorganic reactions of process metallurgy which seemed forty years ago to be completely understood.

This Discussion and its related researches should have considerable repercussions on both physical chemistry and metallurgy. To the physical chemist, research in this field is far more than the application of his technique and knowledge to a particular set of problems, since it brings with it a widening and a modification of his outlook. He is seeing his tools of thermodynamics and reaction kinetics being reshaped and strengthened. Most salutary of all is the way he is forced to re-examine some of his hypotheses whose validity he has taken for granted for so long. Stoichiometry now lets him down so often that he must take another look at what he means by valency. The " ion " which means something real in an aqueous solution takes on a different and perhaps improper guise when the solvent is a metal or a molten silicate. Indeed, the concept of the " molecule," the principal foundation stone of the chemistry of gases becomes unreliable in such systems. The crowning insult comes when we find that a hole or vacant site in a solid is as important, especially in diffusion, as an occupied site !

Fortunately, the destructive process has only upset those parts of our physical chemistry structure where rebuilding will do no harm. We are left with atoms which, at the high temperatures often found in metallurgical processes, recover a great deal of their individuality. Their closed shells of electrons remain fairly inviolate while their valency electrons on the average behave in a manner which is becoming more and more predictable. We have the remnants of molecules such as the silicate units in slags, and with such fundamental principles as that of overall electroneutrality. In rebuilding with our strengthened tools of thermodynamics and reaction kinetics we have a particularly powerful aid in our knowledge of spatial arrangements, ionic radii, etc., derived from X-ray diffraction patterns. We can look forward to the rebuilding of part of the physical chemistry structure on improved lines.

The metallurgist welcomes the increase in factual knowledge as it enables him to reach higher technical achievements and increase the efficiency of his operations. He welcomes the building of models and basic theory provided these are not too complicated for a non-specialist to grasp. The metallurgist is faced with increasing demands for purer metals which means he must " dig down " to lower chemical potentials to remove the impurities. He is faced with the need for more precise control of important alloying elements; this requires better control of his processes and he looks to the physical chemist for help.

I will close with one final impression. The Discussion 23 years ago was exclusively concerned with iron and its alloying elements. This Discussion has broadened considerably into copper, magnesium, aluminium, zinc, etc., but still the balance is much on the ferrous side. This is surprising when it is remembered that the non-ferrous metals have been the chief materials of interest to the metal physicist. It is to be hoped that one of the repercussions of this Discussion will be to bring physical chemistry more strongly into the non-ferrous field.

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